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# GEOCHIMICA ET COSMOCHIMICA ACTA



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# Systematic variation of rare-earth elements in cerium-earth minerals*

K. J. Murata, H. J. Rose jr., M. K. Carron, and J. J. Glass
U.S. Geological Survey, Washington 25, D.C.

(*Received* 17 *May* 1956)

**Abstract**—In a continuation of a study reported previously, rare-earth elements and thorium have been determined in monazite, allanite, cerite, bastnaesite, and a number of miscellaneous cerium-earth minerals. A quantity called sigma ($\Sigma$), which is the sum of the atomic percentages of La, Ce, and Pr, is proposed as an index of composition of all cerium-earth minerals with respect to the rare-earth elements. The value of $\Sigma$ for all of the minerals analysed falls between 58 and 92 atomic per cent. Monazites, allanites, and cerites cover the entire observed range, whereas bastnaesites are sharply restricted to the range between 80 and 92 atomic per cent.

The minimum value of $\Sigma$ for a cerium-earth mineral corresponds to the smallest possible unit-cell size of the mineral. In monazite, this structurally controlled minimum value of $\Sigma$ is estimated to be around 30 atomic per cent. Neodymium, because of its abundance, and yttrium, because of its small size, have dominant roles in contraction of the structure. In the other direction, the limit of variation in composition will be reached when lanthanum becomes the sole rare-earth element in a cerium-earth mineral.

Cerium-earth minerals from alkalic rocks are all characterized by values of $\Sigma$ greater than 80 atomic per cent, indicating that the processes that formed these rocks were unusually efficient in fractionating the rare-earth elements—efficient in the sense that a highly selected assemblage is produced without eliminating the bulk of these elements.

Analyses of inner and outer parts of two large crystals of monazite from different deposits show no difference in $\Sigma$ in one crystal and a slightly smaller value of $\Sigma$ in the outer part of the other crystal compared to the inner part. The $\Sigma$ of monazites from pegmatites that intrude genetically related granitic rocks in North Carolina is found to be either higher or lower than the $\Sigma$ of monazites in the intruded host rock. These results indicate that the fractionation of the rare-earth elements is not a simple unidirectional process.

When a cerium-earth mineral undergoes replacement, its rare-earth elements may be fractionated into two parts, one forming a new mineral with $\Sigma$ that is smaller, and the other a second new mineral with $\Sigma$ that is larger than that of the original mineral.

The complete analysis of a cerium-earth mineral to determine its $\Sigma$ is time consuming. The discovery of a direct relationship between $\Sigma$ and the Ce/(Nd + Y) atomic ratio in cerium earth minerals allows a rapid determination of $\Sigma$ from spectrograms obtained in a previously described method for determining thorium in these minerals.

## Introduction

An attempt was made in a previous study (Murata *et al.*, 1953) to determine the total range of variation in the composition of monazite with respect to the rare-earth elements. To denote the composition of each sample by means of a single number, the quantity $\Sigma$ La + Ce + Pr in atomic per cent of total rare-earth elements was proposed as a numerical index of the composition and of the stage of fractionation attained by the rare-earth elements. This quantity was found to range between 58 and 87 atomic per cent of the total rare-earth elements in ten monazites from widely scattered localities. Subsequent analyses of sixteen other monazites, reported in this paper, give atomic percentages of $\Sigma$ La + Ce + Pr in this same range and confirm the general variation trends previously found for the individual rare-earth elements.

Vainshtein and co-workers (1955) have recently published analyses of twenty three monazites which, upon recalculation to atomic percentage, show $\Sigma$ La + Ce + Pr ranging between 62 and 90 atomic per cent, in good agreement with our result.

* Publication authorized by the Director, U.S. Geological Survey.

Their slightly higher values may be explained in part by the fact that yttrium was not determined in their samples.

Other cerium minerals studied by us include several samples of allanite, bastnaesite, and cerite, and single samples of törnebohmite, gorceixite, burbankite, calkinsite, parisite, and sahamalite. The present study is a part of a general plan to determine the composition of the main rare-earth minerals in order to derive basic geochemical data for the rare-earth elements. Thirty-two years ago Goldschmidt and Thomassen (1924) made such a survey of the rare-earth minerals, but the improved analytical methods now available encourage and justify a resurvey.

## Description of Samples and of the Method of Analysis

The localities of the samples studied are given in Table 1; the numbers of the samples are continued in sequence from our previous paper. The samples were purified by means of heavy liquids and the Frantz magnetic separator, followed by hand picking of the remaining grains of impurities. The purity of the final sample was checked under the unfiltered light of a mercury-vapour lamp with which cerium-earth minerals assume a distinctive green colour (Murata and Bastron, 1956).

The methods of analysis used for determining the individual rare-earth elements and thorium have been described previously (Rose *et al.*, 1954; Dutra and Murata, 1954). A few samples (marked with dagger in Table 2) were available only in milligram quantities, which precluded their analysis by the regular procedures. They were analysed by the method of dilution with pegmatite base (Fleischer *et al.*, 1952), which gives results of somewhat lower precision. The analytical results are given in Table 2 in terms of weight per cent of the total rare earths plus thoria precipitate that was chemically separated from each sample, and in Table 3 in terms of atomic per cent of the total rare-earth elements with thorium excluded.

## Monazite

The atomic percentages of the individual rare-earth elements of the sixteen new samples and of the ten samples previously reported by us have been plotted against $\Sigma$ La + Ce + Pr in Fig. 1. The dashed lines indicate the general trends of the variations and show La and Ce increasing together, and Nd, Sm, Gd, and Y decreasing concomitantly. Praseodymium, occupying an intermediate position in a gradational series, remains nearly constant. As shown in our previous paper, the dashed lines can be calculated on the basis of a process of repeated fractional precipitation of the rare-earth elements.

Deviations from the dashed lines have been ascribed by us to differences in the temperature of formation of the different monazites. Temperature differences are believed to have a greater effect on the solubility of Ce, Pr, and Nd as the phosphate, relative to the other elements. The dashed lines for Ce, Pr, and Nd in Fig. 1 have the interesting property that $\Sigma'$ Ce + Pr + Nd is constant at 69·1 atomic per cent throughout the entire range of $\Sigma$ La + Ce + Pr. Thus this value of $\Sigma'$ Ce + Pr + Nd can be used to define a hypothetical average temperature for the formation of monazite, but at present we have no data to enable us to

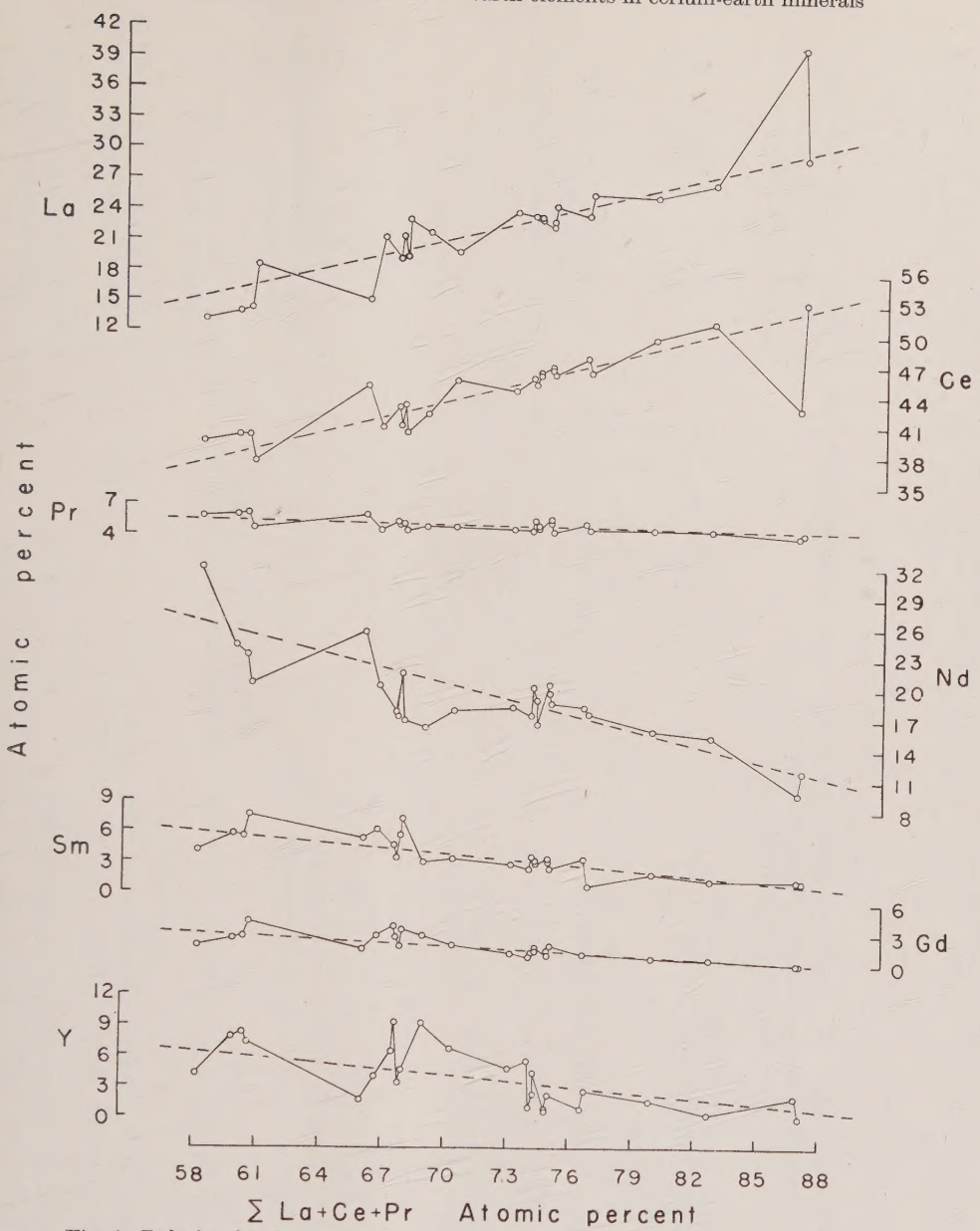



Fig. 1. Relationship between the atomic percentages of the individual rare-earth elements (ordinate) and the sum of the atomic percentages of La, Ce, and Pr (abscissa) for twenty six samples of monazite.

ascribe values higher than 69·1 atomic per cent to abnormally high or low temperatures. We shall, for the present, confine the discussion to the general trends of variations as indicated by the dashed lines, and not consider the deviations from these lines any further.

The differences in the proportions of the rare-earth elements in monazite have been discussed by a number of investigators in terms of the relative abundance

Table 1. Localities of minerals

| No. | Locality | Source rock | Paragenesis | Reference |
|---|---|---|---|---|
| Monazite | | | | |
| 11 | Jamestown, Colorado. Southern group of deposits. | Aplite-pegmatite zones of granite along borders of included schist. | Cuts törnebohmite (no. 39) | Goddard and Glass(1940) |
| 1 | No. 20 mine, Crabtree Creek near Little Switzerland, North Carolina. U.S. Nat. Mus. No. G-5581. | Pegmatite | | |
| 12 | Grama, Sao Paulo, Brazil | Pegmatite | a. Inner part of a large crystal.<br>b. Outerpart of the same crystal. | D. Guimarães, personal communication |
| 13 | Hitterö, Norway U.S. Nat. Mus. R-7154. | Pegmatite | a. Inner part of a large crystal.<br>b. Outer part of the same crystal. | |
| 14 | Yucca Valley, California | Pegmatite | | |
| 15 | Shelby district, North Carolina | Biotite schist | | W. C. Overstreet, personal communication. |
| 16 | Chesterfield County, Virginia | Granite | | J. B. Mertie, jr., personal communication. |
| 17 | Byron Bay, New South Wales, Australia | Beach sand | | Split of sample analysed by Wylie (1950) |
| 18 | Shelby district, North Carolina | Sillimanite schist | | W. R. Griffitts, personal communication. |

| | | | | | |
|---|---|---|---|---|---|
| | 6 | Acre Rock quarry, Shelby district, North Carolina | Main mass of quartz monzonite in quarry | | J. B. Mertie, jr., collector. |
| | 19 | Acre Rock quarry, Shelby district, North Carolina | Main mass of quartz monzonite in quarry. Duplicate sample | | W. C. Overstreet, collector |
| | 20 | Acre Rock quarry, Shelby district, North Carolina | Quartz monzonite pegmatite | Pegmatite intrudes main mass in quarry | |
| | 21 | Quarry near Hollis, Shelby district, North Carolina | Large dike of quartz monzonite | | W. C. Overstreet, collector |
| | 22 | Quarry near Hollis, Shelby district, North Carolina | Quartz monzonite pegmatite | Pegmatite intrudes the large dike in quarry | Keston Teague, collector |
| | 23 | Shelby district, North Carolina | Biotite gneiss | | |
| Allanite | | | | | |
| | 24 | Magnet Cove, Arkansas | Apatite-pyrite dike | | L. V. Blade, personal communication. |
| | 25 | Same as monazite no. 1 | Same as monazite no. 1 | Cuts and replaces monazite no. 1 | |
| | 26 | Same as monazite no. 11 | Same as monazite no. 11 | Last rare-earth mineral to form. | Goddard and Glass, 1940. |
| | 27 | Sulphide Queen ore body, Mountain Pass district, California. | Late-phase carbonate veins in main bastnaesite-barite-carbonate body in schist and gneiss. | | Olson *et al.* (1954), Jaffe (1955). |
| Cerite | | | | | |
| | 28 | Same as monazite no. 11 | Same as monazite no. 11 | First rare-earth mineral to form. | Goddard and Glass (1940) |

Table 1 (*continued*)

| No. | Locality | Source rock | Paragenesis | Reference |
|---|---|---|---|---|
| Cerite | | | | |
| 29 | Bastnäs, Riddarhyttan district, Sweden. U.S. Nat. Mus. No. 60923. | Amphibole skarn in granulite | | Geijer (1921). |
| 30 | Birthday Claims area, Mountain Pass district, California. | No. 6 carbonate vein in shonkinite | | Olson *et al.* (1954). |
| Bastnaesite | | | | |
| 31 | Sulphide Queen ore body, Mountain Pass district, California | Main bastnaesite-barite-carbonate body in schist and gneiss | | Olson *et al.* (1954). |
| 32 | Karonge mine, Ruanda-Urundi, Central Africa. Mus. Belg. Congo No. RG-3103 | Veins in pegmatized schist | | L. S. Cahen, Mus. Belg. Congo, personal communication. |
| 33 | Cheyenne Canyon, Pikes Peak region, El Paso County, Colorado. U.S. Nat. Mus. No. 84413. | Miarolitic pegmatites in granite | | Hillebrand (1899); E. P. Kaiser, personal communication. |
| 34 | Inclined shaft, Birthday-Claims area, Mountain Pass district, California | Carbonate vein in shonkinite | | Olson *et al.* (1954). |
| 35 | Same as cerite no. 30 | Same as cerite no. 30 | Replaces cerite no. 30 | |
| 36 | Red Cloud area, Gallinas Mountains, New Mexico. U.S.Nat.Mus. No. 105628. | Hydrothermal veins of fluorite-barite | | Glass and Smalley (1945). |

| | | | | |
|---|---|---|---|---|
| 37 | Bastnäs, Riddarhyttan district, Sweden. U.S. Nat. Mus. No. 96428. | Amphibole skarn in granulite | | Geijer (1921). |
| 38 | Madagascar. U.S. Nat. Mus. No. R-2617. | Pegmatite? | | Glass and Smalley (1945) |
| Miscellaneous Minerals | | | | |
| 39 | Törnebohmite. Same locality as monazite no. 11. | Same as monazite no. 11 | Replaces cerite no. 28 | Goddard and Glass (1940) |
| 40 | Gorceixite, Bashi, Alabama | Marl with marine fossils and much greensand; of lower Eocene age. | | F. S. MacNeil, personal communication. |
| 41 | Burbankite, Bearpaw Mountains, Montana | Carbonate veins in shonkinite | First rare-earth mineral in veins. | Pecora and Kerr (1953). |
| 42 | Parisite, Sulphide Queen ore body, Mountain Pass district, California | Main bastnaesite-barite-carbonate body in schist and gneiss | Occurs in parallel intergrowths with bastnaesite. Also forms through hydrothermal alteration tion of bastnaesite. | Olson *et al.* (1954) |
| 43 | Sahamalite, Sulphide Queen ore body, Mountain Pass district, California | In a dolomitic part of the main body. | Forms through hydrothermal alteration of bastnaesite. | Jaffe *et al.* (1953). |
| 44 | Calkinsite, Same locality as burbankite no. 41 | Same as burbankite no. 14 | One of the alteration products of burbankite no. 41 | Pecora and Kerr (1953). |

Table 2. Composition in weight per cent of rare-earth plus thoria precipitates separated from cerium-earth minerals

| Mineral | Monazite | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 11 | 1* | 12a | 12b | 13a | 13b | 14 | 15 | 16 | 17 | 18 | 6* | 19 | 20 | 21 | 22 | 23 | 24† |
| $La_2O_3$ | 12·7 | 15·6 | 11·4 | 12·0 | 17·3 | 16·8 | 12·3 | 21·2 | 20·3 | 20·2 | 22·6 | 20·1 | 20·2 | 20·5 | 21·8 | 15·8 | 24·4 | 39 |
| $CeO_2$ | 40·1 | 33·1 | 34·6 | 35·3 | 35·0 | 33·4 | 29·5 | 43·1 | 42·1 | 42·2 | 44·8 | 40·7 | 42·8 | 43·5 | 44·4 | 36·6 | 50·9 | 43 |
| $Pr_6O_{11}$ | 5·9 | 4·1 | 5·2 | 5·3 | 4·0 | 4·1 | 3·2 | 4·3 | 4·3 | 4·6 | 4·2 | 5·0 | 4·9 | 4·7 | 4·2 | 4·6 | 4·4 | 4 |
| $Nd_2O_3$ | 31·8 | 17·8 | 20·6 | 20·1 | 13·0 | 13·8 | 11·3 | 16·2 | 14·8 | 17·1 | 17·4 | 17·9 | 17·6 | 16·2 | 13·9 | 14·9 | 14·5 | 10 |
| $Sm_2O_3$ | 4·3 | 6·9 | 5·1 | 4·9 | 2·5 | 2·9 | 2·2 | 2·3 | 2·9 | 2·8 | 2·3 | 3·3 | 3·2 | 3·1 | 1·7 | 4·1 | 1·2 | 1 |
| $Gd_2O_3$ | 1·9 | 3·8 | 2·3 | 2·5 | 2·3 | 2·3 | 1·3 | 0·7 | 1·5 | 1·4 | 1·9 | 1·1 | 1·1 | 1·0 | 0·7 | 3·4 | 0·5 | 0 |
| $Y_2O_3$ | 2·8 | 4·3 | 4·4 | 4·8 | 5·0 | 5·0 | 2·9 | 3·4 | 2·7 | 1·3 | 1·4 | 0·6 | 0·6 | 0·6 | 0·9 | 3·6 | 0·2 | 2 |
| $ThO_2$ | 1·4 | 12·1 | 16·3 | 15·5 | 19·5 | 21·3 | 36·6 | 7·7 | 11·0 | 11·0 | 6·7 | 10·9 | 7·7 | 9·3 | 13·0 | 17·5 | 6·7 | 0 |
| Total | 100·9 | 97·7 | 99·9 | 100·4 | 98·6 | 99·6 | 99·3 | 98·9 | 99·6 | 100·6 | 101·3 | 99·6 | 98·1 | 98·9 | 100·6 | 100·5 | 102·8 | 99 |

| Allanite | | | Cerite | | | Bastnaesite | | | | | | | | Miscellaneous | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 25 | 26 | 27† | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 |
| 15·2 | 17·2 | 29 | 15·0 | 23·4 | 21·9 | 25·7 | 28·9 | 24·9 | 29·6 | 42·1 | 42·9 | — | — | 10·6 | 16·5 | 25·8 | 29·2 | 28·5 | 30·7 |
| 34·9 | 51·4 | 54 | 42·9 | 48·0 | 54·3 | 49·8 | 48·0 | 52·1 | 50·3 | 44·6 | 45·6 | — | — | 41·2 | 36·8 | 53·6 | 49·3 | 52·4 | 52·0 |
| 4·4 | 5·2 | 4·5 | 5·4 | 5·5 | 5·7 | 4·8 | 4·3 | 5·3 | 4·4 | 3·5 | 3·9 | — | — | 6·1 | 5·9 | 4·2 | 4·2 | 3·9 | 4·5 |
| 18·4 | 22·3 | 13 | 28·1 | 18·0 | 16·1 | 15·6 | 15·1 | 14·3 | 14·3 | 8·4 | 7·1 | — | — | 32·3 | 25·0 | 15·4 | 13·7 | 12·1 | 12·3 |
| 6·4 | 2·1 | 0·3 | 3·4 | 1·6 | 1·5 | 1·8 | 1·3 | 1·0 | 1·3 | 0·8 | 0·5 | — | — | 4·5 | 6·1 | 1·1 | 1·3 | 1·1 | 0 |
| 3·8 | 1·0 | 0·2 | 1·5 | 1·0 | 0·4 | 0·9 | 0·5 | 0 | 0 | 0 | 0 | — | — | 1·4 | 3·9 | 0·8 | 0 | 0 | 0 |
| 4·0 | 1·8 | 0·3 | 3·1 | 0·9 | 0·6 | 0·2 | 0·2 | 0·3 | 0 | 0 | 0·1 | — | — | 2·1 | 4·1 | 1·1 | 0·2 | 0 | 0 |
| 9·8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0·8 | 1·0 | 0 | 0 | 0 | 0 | 0 |
| 96·9 | 101·0 | 101·3 | 99·4 | 98·4 | 100·5 | 98·8 | 98·3 | 97·9 | 99·9 | 99·4 | 100·1 | — | — | 99·2 | 98·3 | 102·0 | 97·9 | 98·0 | 99·5 |

of the more basic and the less basic groups of elements, but usually these two categories of elements have not been defined precisely. Fig. 1 shows that the more basic group can be defined to consist of La, Ce, and Pr, and that this group varies in abundance in the sense opposite to the less basic group that includes the remaining elements. Hence, the quantity $\Sigma$ La + Ce + Pr in atomic per cent specifies the total content of the more basic rare-earth elements in monazite. *This quantity will be referred to below simply as* $\Sigma$.

## General Features of Fractional Precipitation Processes in Nature

The fractional precipitation or deposition of elements from a magma as rock-forming minerals is a familiar concept. The complete precipitation of an element by any single geochemical process is unusual; among the few examples which approach this might be the coprecipitation of divalent nickel in the magnesium minerals of mafic rocks.

Table 3. Composition in atomic per cent of rare-earth elements separated from cerium-earth minerals

| Mineral | Monazite | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 11 | 1 | 12a | 12b | 13a | 13b | 14 | 15 | 16 | 17 | 18 | 6 | 19 | 20 | 21 | 22 | 23 | 24 |
| La | 13·1 | 18·3 | 13·9 | 14·3 | 22·0 | 21·6 | 20·0 | 23·7 | 23·5 | 23·2 | 24·6 | 23·5 | 23·1 | 23·7 | 25·6 | 19·4 | 26·9 | 40 |
| Ce | 39·2 | 36·5 | 39·9 | 39·9 | 42·0 | 40·9 | 45·4 | 45·7 | 46·1 | 46·0 | 46·0 | 45·0 | 46·5 | 47·7 | 49·6 | 42·7 | 51·2 | 43 |
| Pr | 5·8 | 4·6 | 6·0 | 6·1 | 4·9 | 5·1 | 4·9 | 4·6 | 4·7 | 5·1 | 4·4 | 5·6 | 5·3 | 5·2 | 4·7 | 5·4 | 4·6 | 4 |
| Nd | 31·8 | 20·0 | 24·2 | 23·2 | 16·2 | 17·2 | 17·9 | 17·4 | 16·5 | 19·0 | 18·6 | 20·2 | 19·6 | 18·2 | 15·9 | 17·7 | 15·3 | 10 |
| Sm | 4·1 | 7·5 | 5·7 | 5·5 | 3·0 | 3·4 | 3·3 | 2·4 | 3·2 | 3·0 | 2·4 | 3·6 | 3·4 | 3·3 | 1·9 | 4·7 | 1·2 | 1 |
| Gd | 1·8 | 4·0 | 2·5 | 2·7 | 2·8 | 2·6 | 1·8 | 0·7 | 1·6 | 1·3 | 1·8 | 1·1 | 1·1 | 1·0 | 0·7 | 3·7 | 0·5 | 0 |
| Y | 4·2 | 7·2 | 7·8 | 8·3 | 9·1 | 9·2 | 6·7 | 5·5 | 4·4 | 2·3 | 2·2 | 1·0 | 1·0 | 0·9 | 1·6 | 6·4 | 0·3 | 2 |
| ΣLa + Ce + Pr | 58·1 | 59·4 | 59·8 | 60·3 | 68·9 | 67·6 | 70·3 | 74·0 | 74·3 | 74·3 | 75·0 | 74·1 | 74·9 | 76·6 | 79·9 | 67·5 | 82·7 | 87 |
| Ce/(Nd + Y) | 1·09 | 1·34 | 1·25 | 1·27 | 1·66 | 1·55 | 1·84 | 2·00 | 2·20 | 2·16 | 2·21 | 2·12 | 2·26 | 2·50 | 2·83 | 1·77 | 3·28 | 3·6 |

| Allanite | | | Cerite | | | Bastnaesite | | | | | | | | Miscellaneous | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 | 44 |
| 17·8 | 17·6 | 30 | 15·5 | 24·6 | 21·9 | 26·9 | 30·4 | 26·3 | 30·7 | 43·6 | 44·1 | — | — | 10·8 | 17·1 | 26·1 | 30·9 | 30·1 | 31·9 |
| 38·7 | 49·6 | 52 | 41·9 | 47·8 | 53·4 | 49·4 | 47·8 | 52·4 | 49·3 | 43·7 | 44·5 | — | — | 41·1 | 36·3 | 51·4 | 49·4 | 52·4 | 51·2 |
| 5·0 | 5·1 | 4·3 | 5·3 | 5·5 | 5·7 | 4·8 | 4·3 | 5·4 | 4·4 | 3·5 | 3·8 | — | — | 6·2 | 5·9 | 4·0 | 4·2 | 4·0 | 4·5 |
| 20·8 | 22·1 | 13 | 28·1 | 18·2 | 16·2 | 15·7 | 15·4 | 14·5 | 14·4 | 8·4 | 7·0 | — | — | 33·0 | 25·1 | 15·1 | 14·0 | 12·4 | 12·4 |
| 7·0 | 2·0 | 0·3 | 3·3 | 1·6 | 1·5 | 1·7 | 1·3 | 1·0 | 1·2 | 0·8 | 0·5 | — | — | 4·4 | 5·9 | 1·0 | 1·3 | 1·1 | 0 |
| 4·0 | 0·9 | 0·2 | 1·4 | 0·9 | 0·4 | 0·1 | 0·5 | 0 | 0 | 0 | 0 | — | — | 1·3 | 3·6 | 0·8 | 0 | 0 | 0 |
| 6·7 | 2·7 | 0·5 | 4·6 | 1·4 | 0·9 | 1·4 | 0·3 | 0·5 | 0 | 0 | 0·1 | — | — | 3·2 | 6·1 | 1·6 | 0·2 | 0 | 0 |
| 61·5 | 72·3 | 86 | 62·7 | 77·9 | 81·0 | 81·1 | 82·5 | 84·1 | 84·4 | 90·8 | 92·4 | 90 | 92 | 58·1 | 59·3 | 81·5 | 84·5 | 86·5 | 87·6 |
| 1·41 | 2·00 | 4·0 | 1·28 | 2·43 | 3·12 | 2·89 | 3·04 | 3·49 | 3·42 | 5·20 | 6·26 | 5·2 | 6·1 | 1·14 | 1·16 | 3·08 | 3·48 | 4·22 | 4·13 |

* Reanalysis of previously reported samples by means of improved spectrographic standards.
† Small samples analyzed by the method of dilution with pegmatite base.
Zero in unit column means the element was below the sensitivity limit of the spectrographic methods used. Sensitivity limit for $Sm_2O_3$, 0·3; for $Gd_2O_3$, 0·2; for $Y_2O_3$, 0·1; and for $ThO_2$, 0·8 per cent.

Repeated fractional precipitation of the rare-earth elements in the form of various compounds has long been a general laboratory procedure in separating these elements (Yost *et al.*, 1950; and Vickery, 1953). A preferential precipitation of either the more basic or the less basic elements may be obtained, depending on the nature of the compound precipitated.

In nature, rare-earth elements not only are deposited in the form of minerals like monazite and xenotime, but a substantial part of the total quantity is captured by apatite, sphene, fluorite, garnet, pyroxene, epidote, and other rock-forming minerals (Rankama and Sahama, 1950; Wager and Mitchell, 1951). In order to follow the course of fractionation of these elements in detail, it is, therefore, necessary to determine them quantitatively in all of these minerals. At present,

the fractional precipitation of the rare-earth elements can only be discussed as a general process without specifying the nature of the minerals involved.

In calculating the dashed trend lines in Fig. 1, we assumed one of the simplest modes of fractional precipitation in which the less basic of the cerium-earth elements are preferentially precipitated as monazite or some other mineral with like preferences. Such a process is unidirectional, and the mother liquor becomes progressively richer in the more basic elements. This trend could be reversed at any time if minerals with a preference for the more basic rare-earth elements were to start precipitating. As is seen below, such reversals are not uncommon.

In the simple unidirectional scheme that was assumed, the value of $\Sigma$ of a precipitate is always smaller than that of the mixture of the rare-earth elements in the mother liquor. This characteristic is of special interest when a solution of the rare-earth elements is formed through the dissolution of a pre-existing mineral. The first new mineral formed from such a solution may show a lower value of $\Sigma$ than that of the mineral which was dissolved.

## Limits of $\Sigma$ La + Ce + Pr in Monazite

The lowest value of $\Sigma$ found, namely 58 atomic per cent, raises the question whether this is the lowest value possible in monazite, and if so, what factors operate to set this limit. In addition to the twenty six samples studied by us, none of the twenty three samples analyzed by Vainshtein and colleagues (1955) has a lower value.

In laboratory preparations, $\Sigma$ can be reduced to zero because the monazite phase is obtainable with pure $NdPO_4$, as shown by Mooney (1948). Carron, Rose, and Hildebrand of the Geological Survey (personal communication) have further shown that Sm, Eu, and Gd also form phosphates of the monazite phase; the remaining rare-earth elements form the xenotime phase. An important key to the problem of limits of solid solution was found by Schlyter (1953), who synthesized $LaF_3$ and studied the contraction of its unit cell as he substituted the smaller rare-earth ions in the place of lanthanum in the structure. He made the interesting discovery that, regardless of which of the smaller ions he used, the structure of $LaF_3$ became saturated with the substituent when the unit cell contracted to a certain limiting size. The contraction of the structure appears to be a necessary condition for the retention of the smaller ions. When the structure has contracted to the smallest size possible, it loses its power to hold any more of the smaller ions within itself.

The minimum size of the unit cell attainable with the monazite structure is not known precisely, but it is probably close to that of $GdPO_4$, the last of the lanthanide series to form the monazite phase. All of the less basic elements of natural monazite contribute to the contraction of the unit cell down toward the limiting size to a measure dependent on their abundances and ionic radii. Neodymium, because of its abundance, and yttrium, because of its small size, have dominant roles in contracting the unit cell. The effectiveness of the various elements can be calculated in terms of their equivalence to yttrium, by using Schlyter's values ($k$) for relative power of contraction.

In a series of experiments, CARRON, ROSE, and HILDEBRAND (personal communication) have demonstrated that $CePO_4$ (monazite phase) will incorporate a maximum of about 50 atomic per cent of yttrium, if sufficient phosphate is present to insure complete precipitation of the rare-earth elements. The size of the unit cell of such a preparation is very close to that of $GdPO_4$. If there is a substantial deficiency of phosphate, i.e. the precipitation is partial, an entirely different product is obtained which is a xenotime phase consisting mostly of yttrium and a very small percentage of cerium. A rough calculation based on SCHLYTER'S $k$ values and on extrapolation of the dashed lines for the individual elements in Fig. 1 indicates that the experimentally determined maximum content of yttrium in $CePO_4$ is equivalent to a value of $\Sigma$ of about 30 atomic per cent for natural monazites. The lowest value of $\Sigma$ permitted by the structure of monazite, therefore, seems to be considerably smaller than the minimum found to date. This may be viewed as indirect evidence that complete precipitation of rare-earth elements from natural solutions occurs very rarely and that partial precipitations are the rule.

Towards the upper end of the series, as $\Sigma$ approaches 100 atomic per cent, the limit of variation will be determined largely by the properties of these three elements. These surviving elements differ appreciably among themselves in basicity, so the processes that separated all other rare-earth elements away from them would continue to remove the less basic members of the trio preferentially until lanthanum remains as the sole rare-earth element. GOLDSCHMIDT and THOMASSEN (1924), in their pioneering work, recognized that fractionation processes could lead to a high concentration of the element at either end of the rare-earth series, namely lanthanum or lutecium. If such an ultimate composition is reached by means of a process of fractional precipitation, the amount of monazite finally deposited may be very small, and the chance of finding it would be poor. The highest concentrations of lanthanum found in the present study (40 to 44 atomic per cent) are shown by monazite no. 24 and by bastnaesites nos. 35 and 36. In these samples, lanthanum becomes equal to, but does not exceed, cerium.

## ALLANITE

The composition of allanite and the remaining cerium-earth minerals is discussed only in terms of $\Sigma$ because the variations of the individual elements are essentially the same as with monazite. The quantity $\Sigma$ for each sample of these minerals is plotted in Fig. 2. We were most fortunate in our choice of the three samples of allanite, because they proved to be widely different in composition. The data indicate that the range of variation of the rare-earth elements in allanite is at least as great as that of monazite.

## CERITE

The range of variation of the rare-earth elements for the three samples of cerite lies between $\Sigma$ values of 63 and 82 atomic per cent, and this substantially approaches the range shown by monazite. Although more samples will have to be analysed to determine the full range, the data already suggest that this could be as great as that of monazite.

### Bastnaesite

In sharp contrast to the minerals discussed above, bastnaesite has a very restricted range of variation of the rare-earth elements. Σ exceeds 80 atomic per cent in every sample analysed, and attains the highest value found among all minerals, namely, 92 atomic per cent. Although the number of samples studied is small, it must be remembered that nearly all of the major localities for this mineral (Glass and Smalley, 1945) are represented. At several of the localities, bastnaesite is found within alkalic rocks or derivative rocks such as carbonatite. As is discussed below, all cerium-earth minerals of such an occurrence show very high values of Σ, so the rare-earth composition of certain of the bastnaesites might be correlated in a general way with the peculiar geochemistry of alkalic rocks. But some bastnaesites, for example, sample no. 33 from xenotime-bearing pegmatites in Cheyenne Canyon near Pikes Peak, Colorado (Penfield, 1893; Hillebrand, 1899) were formed in other geological environments. Thus values of Σ in excess of 80 atomic per cent appear to be an inherent characteristic of the mineral.

There is an interesting suggestion here that the crystal structure of bastnaesite may not be as tolerant of differences in the size of the rare-earth ions as are the structures of the other minerals and that the structure has a strong preference for the larger ions. Such a narrow tolerance is unusual in mineral structures, so the question needs further study.

Following past practice this high concentration of La, Ce, and Pr might be called the bastnaesite type of assemblage of the rare-earth elements. However, the definition of a type of an assemblage in terms of a range of values of Σ in atomic per cent seems to be a more precise and, at the same time, a more general method of designating the composition of cerium-earth minerals.

### Miscellaneous Minerals

A number of single samples of cerium-earth minerals have been analysed by us in the past two years, mostly in connection with mineralogical investigations by others. The analyses are compiled in Tables 2 and 3 and plotted in Fig. 2. The data are of interest to the present discussion in two respects (1) the values of Σ found do not exceed the range already established, and (2) minerals from alkalic rocks are in agreement with all others from such rocks in having values of Σ greater than 80 atomic per cent.

### Cerium-earth Minerals from Alkalic Rocks

In Fig. 2, minerals from alkalic rocks or from carbonatites associated with alkalic rocks are designated by black circles. The localities represented are Magnet Cove, Arkansas; the Mountain Pass bastnaesite district, California; and Bearpaw Mountains, Montana. All of these samples are characterized by values of Σ in excess of 80 atomic per cent. As previously noted, bastnaesite apparently contains these high proportions of La, Ce, and Pr irrespective of the type of rock in which it occurs. Thus, it is the composition of minerals like monazite, allanite, and cerite, which are known to vary more widely in composition that provides the most satisfactory evidence as to the nature of the rare-earth elements in alkalic rocks.

The four samples of these minerals (nos. 10, 24, 27, 30) from alkalic rocks all have $\Sigma$ in excess of 80 atomic per cent, suggesting that the preponderance of the more basic rare-earth elements is truly characteristic of such rocks. Alkalic rocks are also notably lacking in yttrium-earth minerals. The predominance of the most basic of the rare-earth elements in alkalic rocks has been noticed previously by GOLDSCHMIDT and co-workers (1933), HABERLANDT (1947) and others.

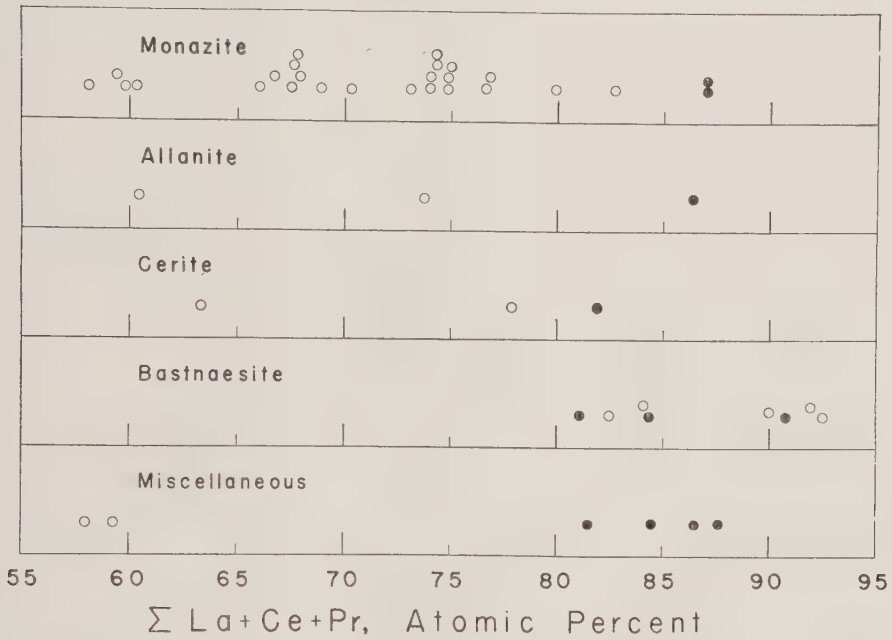



Fig. 2. Composition of cerium-earth minerals in terms of $\Sigma$, the sum of the atomic percentages of La, Ce, and Pr. Black circles designate samples from alkalic rocks; open circles designate samples from granitic rocks, pegmatites, metamorphic rocks, hydrothermal veins, and a marl.

Thus, the rare-earth elements emphasize the peculiarity of the geochemistry of alkalic rocks and may eventually provide valuable clues as to the origin of these rocks. The idea that alkalic rocks are an end-product of a long process of magmatic differentiation, in which the rare-earth elements were subjected to repeated fractional precipitations, would suggest that deposits of rare-earth minerals associated with such rocks might be very small. The large size and richness of the bastnaesite deposit at Mountain Pass, California, seem to contradict such an idea based on a normal scheme of differentiation. The processes that form alkalic rocks appear to be unusually efficient in fractionating the rare-earth elements—efficient in the sense that a highly selected assemblage is produced without sacrificing the bulk of these elements.

Monazites no. 22 ($\Sigma = 80$) and no. 23 ($\Sigma = 83$) are found in concentrations of a few parts per million in quartz monzonite and biotite gneiss, respectively, of the Shelby district of North Carolina. These samples show that a high degree of fractionation of the rare-earth elements may be attained not only in alkalic rocks but in other types of rocks as well, although less commonly.

## Variation of Rare-earth Composition within Single Crystals of Monazite

Analysis of inner and outer portions of large crystals of monazite (3 to 6 cm in diameter) have been made to determine the nature and degree of variation with respect to the rare-earth elements that could occur during the period of growth of single crystals. Samples 12a and 12b represent inner and outer parts of a large crystal from a pegmatite near Grama, Brazil, and their $\Sigma$ are 59·8 and 60·3 atomic per cent, respectively. These values are identical within the error of analysis and show that the rare-earth composition of the magma remained essentially constant during the period of growth of this crystal.

The outer part of the Hitterö crystal (sample 13b) has a value of $\Sigma$ that is 1·3 atomic per cent smaller than that of the inner part (sample 13a). The Ce/(Nd + Y) atomic ratios (whose relationship to $\Sigma$ is explained in the last section of this paper) also indicate that this small negative difference in composition between the earlier and later formed parts of the crystal is real. The sign of the difference is contrary to what would be expected on the basis of the assumed fractional precipitation process.

## Monazites from Different Facies of Toluca Quartz Monzonite

The natural fractionation of the rare-earth elements could also be studied by analysing monazites from two or more genetically related rocks, such as successive differentiates from a batholith or zones of a well-zoned pegmatite. Monazites of such an occurrence are extremely hard to find. Fortunately, Griffitts and Overstreet (1952), in their study of the monazite-bearing Toluca quartz monzonite of North Carolina, obtained monazites from this rock and from a quartz monzonite pegmatite intruding the rock, at two localities (samples 17, 18, 19, 20). Sample 6, from the same locality as sample 17, was furnished by J. B. Mertie jr., and sample 22 was collected by Keston Teague.

Samples 6 and 17 were collected at different times from a large body of the quartz monzonite exposed at Acre Rock quarry in the Shelby district of North Carolina. Sample 18 was obtained from a quartz monzonite pegmatite that intrudes the main body at Acre Rock quarry. Sample 19 was from a large dike of quartz monzonite exposed in a quarry near Hollis, Rutherford County, about sixteen miles west-south-west of the Acre Rock quarry. Sample 20 was from a pegmatite that intrudes this dike rock at the quarry. At both localities, the pegmatite is assumed to be a later differentiate of the magma that produced the main body of quartz monzonite.

The pegmatite monazite (no. 18) from the Acre Rock quarry has a value of $\Sigma$ that is 2·4 atomic per cent higher than the monazites (nos. 6 and 17) from the quartz monzonite at that quarry. This change in composition is in the direction to be expected on the basis of the assumed fractionation process. The pegmatite monazite (no. 20) from the quarry near Hollis, on the other hand, is lower in $\Sigma$ by 12·4 atomic per cent than the monazite from the quartz monzonite at the same quarry, indicating a profound change in rare-earth composition of the magma in the reverse direction.

The data on the large single crystals reported in the previous section and information derived from monazites out of the Toluca quartz monzonite and its accompanying pegmatites, all show that the fractionation of the rare-earth elements in nature is not a simple unidirectional process that leads to a steady increase of the more basic elements in the residual magma. It is apparent that many more genetically related samples need to be studied and also that the nature and degree of fractionation effected by all minerals that deposit rare-earth elements from the magma need to be determined.

## Replacement Reactions among Cerium-earth Minerals

In deposits that contain more than one cerium-earth mineral, certain of these minerals may have formed from others through replacement. The later mineral may or may not have the same proportions of the rare-earth elements as the earlier mineral it replaced, depending on whether fractionation occurred and whether the reaction took place in a closed system. It is evident that replacement reactions could be very complex and difficult to interpret; nevertheless, this aspect of the geochemistry of the rare-earth elements needs to be investigated. The compositions of some of the minerals involved in replacement reactions have been plotted in Fig. 3 in order that the changes in composition may be followed most easily.

Allanite no. 25 ($\Sigma = 61$), from a pegmatite near Little Switzerland, North Carolina, cuts and replaces monazite no. 1 ($\Sigma = 59$). The analysed samples of both minerals were obtained from a single large hand specimen, The value of $\Sigma$ of the replacing mineral is slightly greater than that of the replaced mineral, but the difference is so small that we can conclude that this pair of minerals represents an example of a replacement reaction in which there was very little fractionation of the rare-earth elements. As is seen below, such examples are rare. The total rare-earth content of the allanite is only about a third of that of the monazite, so, if at any given spot the replacement is on the basis of constant volume, a considerable part of the rare-earth elements from the monazite must be mobilized during the reaction to be deposited elsewhere, possibly as more allanite.

Goddard and Glass (1940) have described a complex vein of cerium earth minerals, only about 8 in. thick, at an aplite-schist contact near Jamestown, Colorado. This vein contains cerite no. 28, törnebohmite no. 39, monazite no. 11, allanite no. 26, and a minor amount of bastnaesite. According to Goddard and Glass, cerite was probably the first mineral to crystallize and may at one time have occupied most of the vein. Cerite was extensively replaced by törnebohmite, which in turn was veined irregularly by minor amounts of monazite. The contact of monazite with törnebohmite is said to be sharp, suggesting that monazite was not necessarily a replacement product of törnebohmite. Allanite, the last mineral to form, extensively replaced törnebohmite, residual cerite, and the aplite bordering the vein. The appreciable differences in the rare-earth composition between certain of these minerals are well shown in Fig. 3 (black circles). Unfortunately, bastnaesite, which is present in small amount in the cerite, could not be recovered in a pure form, so its composition could not be determined.

The paragenesis of the minerals in the vein may be summarized according to

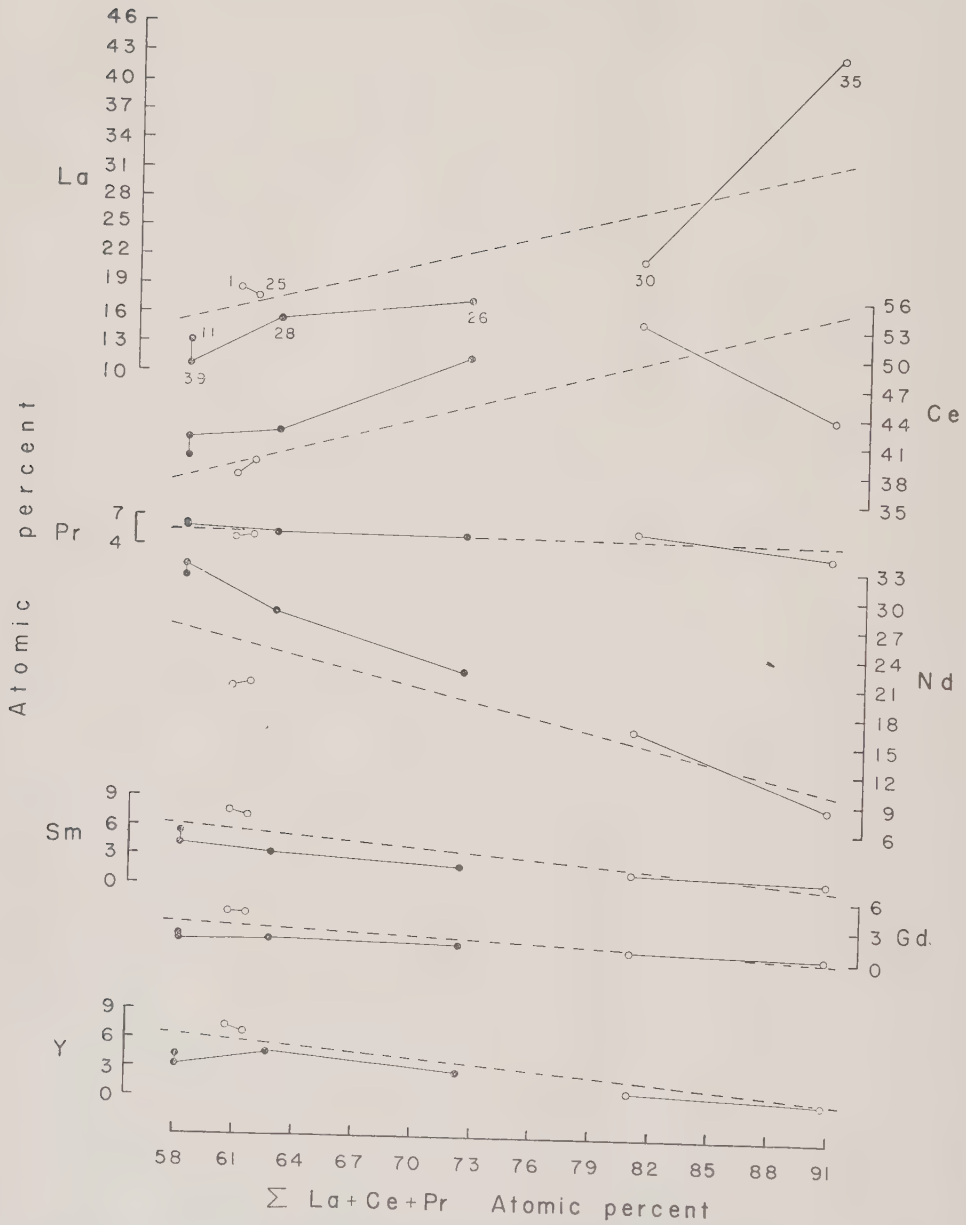
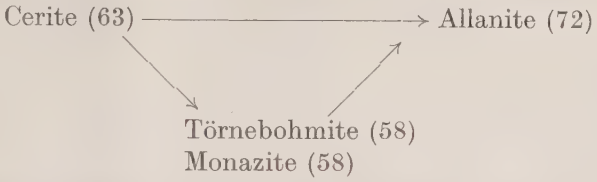



Fig. 3. Composition of cerium-earth minerals that were formed through replacement of pre-existing cerium-earth minerals. The dashed lines denoting the general trends of the variations are the same as those in Fig. 1. The sample number is marked beside the point for percentage of lanthanum.

the following diagram, in which the Σ value of each mineral is given in parenthesis




It is evident that later solutions dissolved and fractionated the rare-earth elements of cerite into two parts, one with the lower value of Σ, which became deposited as törnebohmite and monazite, and the other with the higher value of Σ, which subsequently became deposited as allanite. To this extent, there is good correlation between rare-earth composition and paragenesis. The changes that occurred when törnebohmite in turn was replaced by allanite are not clear. Unfortunately, we could not prepare the allanite formed at the expense of cerite and that formed at the expense of törnebohmite as separate samples; our sample is a composite of all allanite in the vein.

The bastnaesite deposit of the Mountain Pass district, California, is another locality where several different cerium-earth minerals are found (Olsen *et al.*, 1955). Most of the samples that we have analysed were collected for other purposes from widely scattered parts of the district, and their paragenetic relationships are known only in a general way. The analyses of the three samples of bastnaesite (no. 31, 34, and 35) show how Σ (81 to 91) varies even for a single mineral within the district.

Bastnaesite no. 35 (Σ = 91) was formed through the replacement of cerite no. 30 (Σ = 81) in the no. 6 vein of the Mountain Pass district. The value of Σ is considerably higher in the replacing mineral than in the replaced mineral. Here, the possible preference of bastnaesite for the more basic elements may have been an important factor in producing the difference in Σ between the two minerals.

Further studies of other suites of minerals that have formed through replacement are needed to establish the patterns of change in the proportions of the rare-earth elements. The few examples discussed above already show that the changes in a composition can be substantial and, when properly understood, may throw light on the chemistry of mineral replacement.

In Fig. 3, the atomic percentages of the individual rare-earth elements in the four minerals from the Jamestown, Colorado, vein are seen to lie consistently above or below the dashed lines that mark the general trends of fractionation of the individual elements. As previously noted, such deviations signify to us abnormal temperatures of deposition. The abnormal temperature may have prevailed only when cerite was initially deposited. The succeeding minerals may have inherited the deviant proportions from cerite because, in general, the process of fractional precipitation can neither produce nor remove such deviations.

## A Rapid Method for Determining Σ La + Ce + Pr

The quantity Σ has proved to be a very useful designation of the composition of cerium-earth minerals. Making a complete analysis of the chemically separated rare earths (Rose *et al.*, 1954) to determine Σ is time consuming, however, so a

search was made for a more rapid method. An indirect method has been found which takes advantage of spectrograms that are exposed in the spectrographic determination of thorium in cerium earth minerals.

From Fig. 1 it is evident that a ratio of two elements like cerium and neodymium which have divergent trends in the fractionation process, would be a sensitive index of the value of Σ. In Fig. 4 the Ce/Nd atomic ratio of every sample analysed

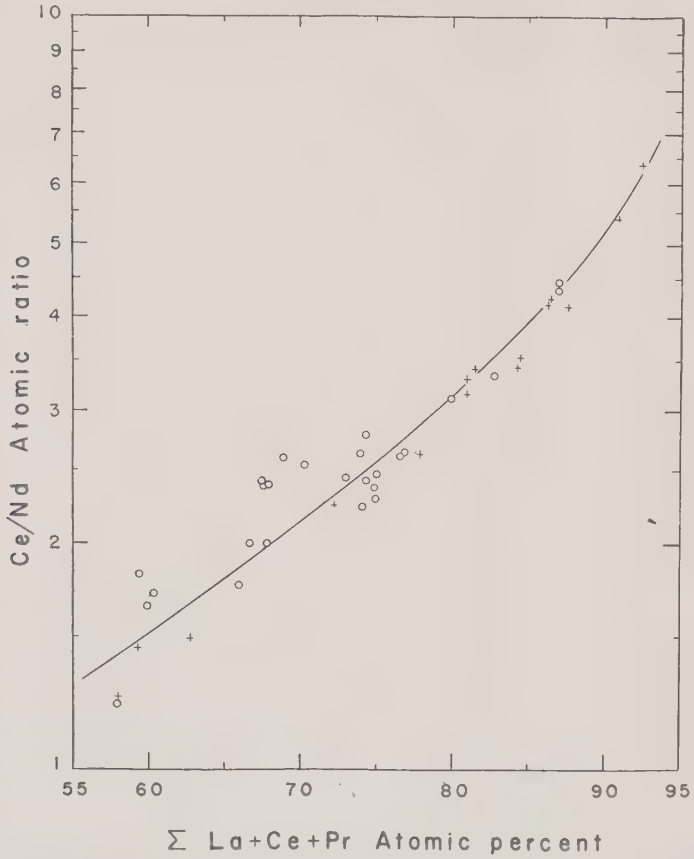



Fig. 4. Relationship between the Ce/Nd atomic ratio and the sum of the atomic percentages of La, Ce, and Pr in cerium-earth minerals. Circles denote monazites; crosses, other cerium-earth minerals.

to date has been plotted against the Σ of the same sample. A fairly good correlation is apparent, but the scatter of points is too great for the relationship to be useful quantitatively.

It was noticed that nearly all of the samples that show large negative deviations of Σ from the average curve in Fig. 3 contain appreciable amounts of yttrium. This element was, therefore, incorporated into an atomic ratio, Ce/(Nd + Y), which is shown plotted against Σ in Fig. 5. The largest deviation of Σ from the best line through all of the points in Fig. 5 is only 3 atomic per cent, and the great majority of the deviations are less than 2 atomic per cent. This relationship, therefore, offers a rapid, sufficiently accurate means of determining Σ, apparently

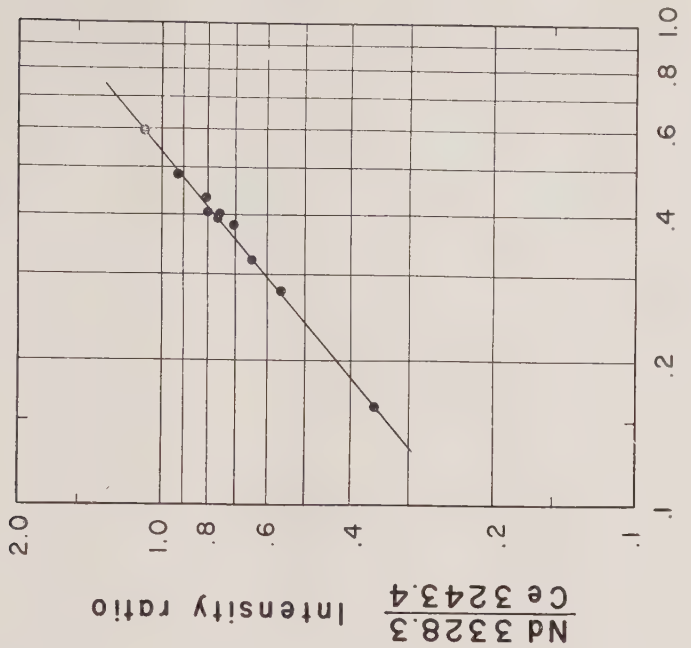



Fig. 6. Analytical curve for the spectrochemical determination of the Nd/Ce atomic ratio in cerium-earth minerals.

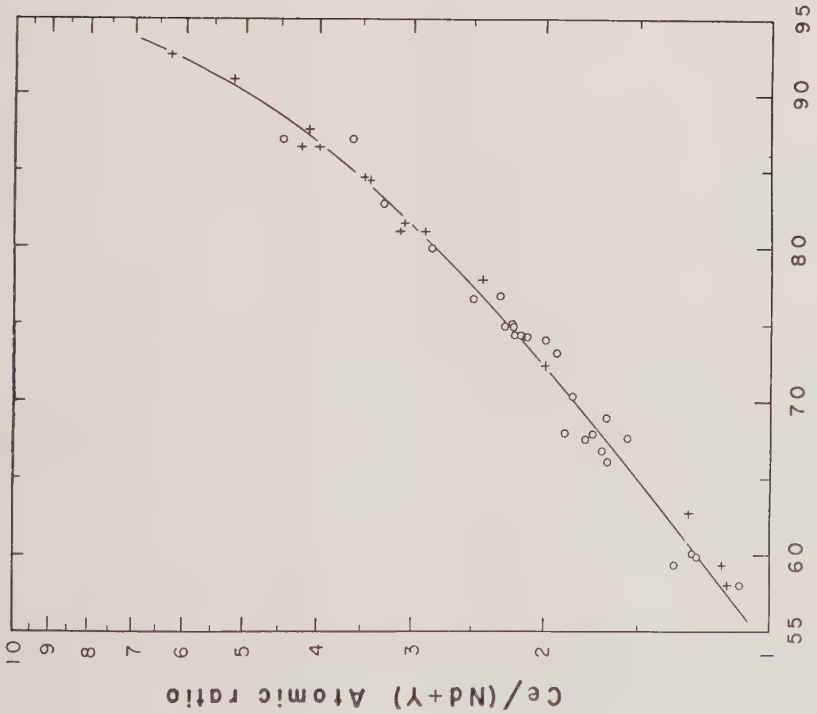



Fig. 5. Relationship between the Ce/(Nd + Y) atomic ratio and the sum of the atomic percentages of La, Ce, and Pr in cerium-earth minerals. Circles denote monazite; crosses, other cerium-earth minerals.

in any cerium-earth mineral. In our current efforts to correlate the composition of monazite from the Shelby quadrangle, North Carolina, with the nature of the source rocks, the values of Σ of the many samples involved are being determined through the use of Ce/(Nd + Y) atomic ratios.

The Ce/(Nd + Y) atomic ratios are determined from spectrograms prepared from determining thorium in cerium-earth minerals (Dutra and Murata, 1954)

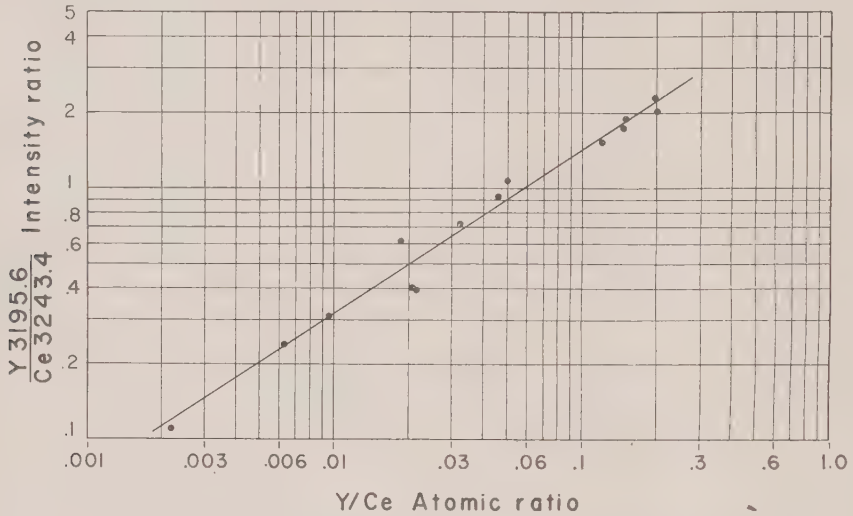



Fig. 7. Analytical curve for the spectrochemical determination of the Y/Ce atomic ratio in cerium-earth minerals.

by microphotometering the Ce-II line at 3243·370 Å, the Nd-II line at 3328·270 Å, and the Y-II line at 3195·615 Å. The Nd/Ce and Y/Ce atomic ratios for each sample are first obtained from the analytical curves given in Figs. 6 and 7. These curves were established by means of the analysed minerals listed in Table 3. The two atomic ratios are then added together and the inverse of the sum is the atomic ratio Ce/(Nd + Y). The value of Σ for the sample is finally read off from the curve given in Fig. 5. The standard deviation for a single determination of the Ce/(Nd + Y) atomic ratio is ±0·10.

*Acknowledgements*—In addition to persons mentioned in the text and tables, we are indebted to George Switzer and W. F. Foshag of the U.S. National Museum for samples used in this study. We also gratefully acknowledge helpful discussions with Kalervo Rankama of the University of Helsinki and with H. T. Evans jr., Michael Fleischer, W. R. Griffitts, C. R. Naeser, and W. C. Overstreet of the Geological Survey.

## References

Dutra C. V. and Murata K. J. (1954) Spectrochemical determination of thorium in monazite by the powder-d.c. arc technique *Spectrochim. Acta* **6,** 373–382.

Fleischer Michael, Murata K. J., Fletcher J. D., and Narten P. F. (1952) Geochemical association of niobium and titanium *U.S. Geol. Survey Circular* **225,** 2–3.

Geijer Per (1921) The cerium minerals of Bastnas at Riddarhyttan *Sveriges Geol. Undersökning* 1921, *Arsbok* 14, no. 6, 24.

Glass J. J. and Smalley R. G. (1945) Bastnäsite *Amer. Mineral.* **30,** 601-615.

Goddard E. N. and Glass J. J. (1940) Deposits of radioactive cerite near Jamestown, Colorado *Amer. Mineral.* **25,** 381–404.

Goldschmidt V. M. and Thomassen L. (1924) Geochemische Verteilungsgesetze der Elemente III, Roentgenspektrographische Untersuchungen ueber die Verteilung der seltenen Erdmetalle in Mineralen *Videnskaps Skrift. Oslo, I, Mat.-Naturv. klasse, no.* **5,** 1–50.

Goldschmidt V. M., Hauptmann H., and Peters C. (1933) Ueber die Bereucksichtigung Seltener Elemente bei Gesteins-Analysen *Naturwissenschaften, Jahrg.* **21,** 362–365.

Griffitts W. R. and Overstreet W. C. (1952) Granitic rocks of the western Carolina Piedmont *Amer. J. Sci.* **250,** 777–789.

Haberlandt H. (1947) Die Bedeutung der Spurenelemente in der geochemischen Forschung *Akad. Wiss. Wien, Math.-naturwiss. Kl., Sitzungsber. Abt.* IIb, Bd. **156,** 293–323.

Hillebrand W. F. (1899) Analyses of tysonite, bastnaesite, prosopite, jeffersonite, covellite, etc. *Amer. J. Sci.* (**4**) 7, 51–52.

Jaffe H. W. (1955) Precambrian monazite and zircon from the Mountain Pass rare-earth district, San Bernardino County, California *Geol. Soc. Amer. Bull.* **66,** 1247–1256.

Jaffe H. W., Meyrowitz Robert, and Evans H. T. jr. (1953) Sahamalite, a new rare earth carbonate mineral *Amer. Mineral.* **38,** 741–754.

Mooney R. C. L. (1948) Crystal structures of a series of rare earth phosphates *J. Chem. Physics* **16,** 1003.

Murata K. J. and Bastron Harry (1956) A convenient method for recognizing nonopaque cerium earth minerals *Science* **123,** No. 3203, 888–889.

Murata K. J., Rose H. J. jr., and Carron M. K. (1953) Systematic variation of rare earths in monazite *Geochim. et Cosmochim. Acta* **4,** 292–300.

Olson J. C., Shawe D. R., Pray L. C., and Sharp W. N. (1954) Rare-earth mineral deposits of the Mountain Pass district, San Bernardino County, California *U.S. Geol. Survey Prof. Paper* 261.

Pecora W. T. and Kerr J. H. (1953) Burbankite and calkinsite, two new carbonate minerals from Montana *Amer. Mineral.* **38,** 1169–1183.

Penfield S. L. (1893) Mineralogical notes. Xenotime from Cheyenne Mountain, El Paso County, Colorado *Amer. J. Sci.* **45,** 398–399.

Rankama Kalervo and Sahama Th. G. (1950) *Geochemistry* Univ. Chicago Press, 508–532.

Rose H. J. jr., Murata K. J., and Carron M. K. (1954) A chemical-spectrochemical method for the determination of rare earth elements and thorium in cerium minerals *Spectrochim. Acta* **6,** 161–168.

Schlyter Kurt (1953) On the coprecipitation of lanthanum ions and tri- or tetrapositive ions as fluorides *Arkiv. Kemi, Bd.* **5,** 61–71.

Vainshtein E. E., Tugarinov A. I., and Turanskaya N. V. (1955) The distribution of the rare earths in monazites *Doklady Akad. Nauk. S.S.S.R.* **104,** 268–271.

Vickery R. C. (1953) *Chemistry of the Lanthanons* Academic Press, N.Y., 296.

Wager L. R. and Mitchell R. L. (1951) The distribution of trace elements during strong fractionation of basic magma—a further study of the Skaergaard intrusion, East Greenland *Geochim. et Cosmochim. Acta* **1,** 129–208.

Wylie A. W. (1950) Composition of some Australian monazites. *Australian J. Appl. Sci.* Vol.1 164–171.

Yost D. M., Russell Horace jr., and Garner C. S. (1947) *Rare-earth Elements and Their Compounds* John Wiley and Sons, N.Y., 92 p.

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# A search for variations in the relative abundance of the zinc isotopes in nature*

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(*Received* 9 *July* 1956)

**Abstract**—The ratio $Zn^{64}/Zn^{68}$ was studied in 18 samples of 7 different zinc minerals. No variations could be detected. If they exist they are less than 0·1% of the ratio.

## Introduction

In recent years variations in the relative isotopic abundances have been observed in many light elements. It is important to see if some of the heavier elements also show variations. Zinc might be suitable for such an investigation because it occurs in minerals formed under very different conditions. Therefore we have measured 18 samples representing seven different minerals and coming from very different localities.

## Chemical Preparation of the Samples

Originally it was decided to use metallic zinc in the mass spectrometer, but $ZnBr_2$ was found to be more convenient and the zinc metal samples were thereafter converted to bromide. All operations were made practically quantitatively and about one gramme of elementary zinc was prepared from each sample.

*Procedure.* The mineral samples were brought into solution by means of a suitable acid, most frequently hydrochloric acid or aqua regia. The other constituents of the zinc minerals and the chemical elements of contaminating intermixed minerals were removed according to the following methods:

Silica was vaporized on a steam bath by treating the samples with hydrofluoric and perchloric acids.

Cadmium, copper, lead, mercury, and arsenic were precipitated by hydrogen sulphide under proper conditions of pH and temperature.

Iron, aluminium, gallium, indium, and thallium were separated by precipitation—if necessary twice—with ammonia after small amounts of $NH_4Cl$ had been added (indicator bromthymol blue). If one or several of these elements were present in larger amounts, the described procedure was preceded by precipitation according to the basic acetate method.

Finally the zinc was purified from cobalt and maganese by inverted precipitation in a strong NaOH solution after a very small quantity of hydrogen peroxide had been previously added to the zinc salt solution.

In order to obtain a compound suitable for electrolysis the zinc salt solutions were—after removal of the ammonium salts—neutralized with sodium hydroxide. Diluted sodium carbonate solution was then slowly added until phenolphthalein changed its colour indicating the pH at which the precipitation of zinc carbonate is as complete as possible. The zinc carbonate was dissolved in formic or acetic acid, the solution evaporated to dryness on a steam bath and the residue dissolved in 100 ml 1% formic or acetic acid. The strength of the acids

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was buffered by adding 5 g of sodium formate or 5 g of sodium acetate respectively. The zinc solutions were now electrolysed using a platinum rod as cathode and a platinum gauze wire cylinder as anode. The temperature was allowed to rise gradually during the electrolysis from about 20°C to about 60–70°C; the current increased at the same time to about 1 A and the electrode potential to 6 V.

After rapid washing with water, alcohol, and ether, and drying at room temperature in a vacuum desiccator, the zinc deposits were dissolved in a mixture of hydrobromic acid and bromine, the latter added in order to decrease effervescence by hydrogen-gas evolution. The zinc bromide solutions were then evaporated to dryness on a steam bath and in order to drive off the water as completely as possible they were dried in an oven at 200°C.

## Mass Spectrometer Measurements

To begin with, metallic zinc was used in the mass spectrometer. This method had the disadvantage that zinc forms a conducting layer on the insulators of the ion source. This sort of trouble could be greatly reduced by using zinc bromide instead of metallic zinc, and by keeping the instrument at about 250°C during operation.

In principle the measurements were made according to the method of Taylor (1954). In this method the compared isotopes have to give the same peak height on a recorder. The rarer isotope is used as a reference and the accuracy obtainable in reading off the recorder is about 0·1%. In the present case the isotopes $Zn^{64}$ and $Zn^{68}$ have been compared, where $Zn^{68}$ is the rarer isotope.

The identities of the samples were not known to the operator. After every second unknown sample a standard sample was run. The results were furthermore checked by a large number of control runs.

## Results and Conclusion

The samples studied are presented in the following table.

| Mineral | Locality |
|---|---|
| Sphalerite, g 2446* | Picos de Europa, Santander, Spain |
| Sphalerite, g 2493 | near Joplin, Missouri, USA |
| Sphalerite, g 2455 | Hunneberg, Västergötland, Sweden |
| Sphalerite, g 2497 | Kef-Oum-Heboul, Algeria |
| Sphalerite, 12055 | Mundijong, SW Division, W. Australia |
| Sphalerite, g 2507 | Nordmarken, Sweden |
| Sphalerite, g 2494 | Ivigtut, Greenland |
| Sphalerite, 061105 | Brevig, Norway |
| Sphalerite, 31654 | Väne-Ryr, Sweden |
| Sphalerite, 170050 | Dannemora, Sweden |
| Zincite, g 6511 | Franklin, NJ, USA |
| Franklinite, g 7676 | Franklin, NJ, USA |
| Gahnite, 061558 | Falun, Sweden |
| Willemite, 333857 | Franklin, NJ, USA |
| Willemite, 31006 | Excelsior Zinc Mine, Lusaka, N. Rhodesia |
| Hemimorphite, g 19363 | Tarnowitz, Silesia |
| Hemimorphite, 470233 | El Potosi Mine, Santa Eulalia, Chihuahua, Mexico |
| Adamite, 470232 | Ojuela Mine, Mapimi, Durango, Mexico |

* Numbers refer to the collection in the Swedish Museum of Natural History.

It is evident that the selection is not complete, the most obvious material lacking being the proteins containing zinc. However, the sphalerites represent the whole temperature range in which this substance can be formed and both primary and secondary zinc minerals from ore deposits are represented.

In this material no variations in the ratio $Zn^{64}/Zn^{68}$ have been observed, i.e. if they exist they must be smaller than 0·1% of the ratio.

*Acknowledgement*—The mass spectrometric measurements have been carried out by Mr. S-E. Säls.

## Reference

Taylor C. (1954) *Arkiv för fysik* **8**, 201–210.

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# Natural variations in the relative abundances of the nitrogen isotopes*

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(*Received* 9 *July* 1956)

**Abstract**—Two samples of $NH_4Cl$, two of caliche, eight of Wealden coal, five of Carboniferous coal, three of living trees and one air sample were studied. The $NH_4Cl$ samples formed a distinct group about 1% heavier than the air sample. The other samples showed variations of some parts per thousand from the air sample. The Wealden-coal nitrogen is heavier than the Carboniferous-coal nitrogen, this being contrary to the results found for the carbon isotopes.

## Introduction

Variations in the stable isotope ratios of light elements have been studied intensely in recent years. As no detailed isotope studies seemed to have been made on nitrogen at the time that this investigation was being planned it was started in order to obtain some idea of the magnitude of possible variations.

Nitrogen consists of two stable isotopes, $N^{14}$ and $N^{15}$, the latter of which is rare (about 0·37%). White and Yagoda (1950) studied nitrogen in uraninites and found a strong age effect in the isotope ratio. However, according to Ingerson (1953) their results have not been confirmed. In 1951 Smith and Hudson studied two samples of crude oil and two samples of coal with ages varying from Cretaceous to Devonian, using tank nitrogen as a reference. They could not with certainty observe any variations and, in particular, no age effect. At the Pennsylvania State University symposium on Nuclear Geophysics in September 1955 T. C. Hoering, Arkansas, and the present writers could present in the main identical results (cf. Hoering, 1955).

## Chemical Methods

The nitrogen-containing materials investigated are salammoniac ($NH_4Cl$), caliche, and organic substances like coal and wood. They were all converted into one single compound $(NH_4)_2SO_4$.

Each substance was first analysed chemically in order to find out how much material was needed to obtain 0·5–0·8 grams of $(NH_4)_2SO_4$. The organic substances were burnt quantitatively according to the Kjeldahl method and the ammonia formed distilled into 25 ml of $1NH_2SO_4$. Pyrex glass apparatus with standard joints was used. The excess $H_2SO_4$ was neutralized with $Ba(OH)_2$ solution using methyl red as indicator. The titration was stopped when the solution turned yellow, and back titration was carried out with $0{\cdot}5\,NH_2SO_4$, drop by drop, until the colour of the indicator changed to red again. The $BaSO_4$ precipitate was filtered off and the clear filtrate, now containing only $(NH_4)SO_4$ solution, was evaporated to a small volume of about 1-2 ml. Then 100 ml of 96% alcohol were slowly added while stirring. After some hours the alcohol, in which the indicator is soluble, was carefully decanted and the $(NH_4)_2SO_4$ precipitate was washed with 50 ml of 96% alcohol once more and decanted. It was then

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washed three times with 50 ml of ethyl ether. The precipitate was dried and sent to the mass-spectrometer laboratory.

Nitrates were reduced to $NH_3$ both with iron and zinc in acid solution and with Devarda's metal in alkaline solution. Before the Devarda reduction the material had been extracted for nitrates with hot water. The $NH_3$ was distilled and treated in the same way as above. The ammonium chloride was distilled direct.

In order to obtain a sample of atmospheric nitrogen completely free from oxygen a pyrogallol solution was used, with white phosphorus subsequently removing the last traces. Finally the sample was dried over $P_2O_5$.

## Mass Spectrometric Measurements

Nitrogen gas for measurement in the mass spectrometer was prepared from the $(NH_4)_2SO_4$ samples according to the method described by Sprinson and Rittenberg (1949). The mass spectrometer used was a 180° double-collector instrument of the Nier type. The identity of each sample was unknown to the operator. The measurements have been referred to a standard sample of $(NH_4)_2SO_4$ and the recorded masses are 28 and 29. The values presented in the tables are

$$\delta = \frac{\mathrm{N}(29)/\mathrm{N}(28)\ \text{air} - \mathrm{N}(29)/\mathrm{N}(28)\ \text{air}}{\mathrm{N}(29)/\mathrm{N}(28)\ \text{air}} \times 1000$$

A positive value indicates that the sample contains more $N^{15}$ than the air sample.

Unfortunately the accuracy was not as good as might have been expected because the mass spectrometer had to be used for other series of biological $N^{15}$-enriched samples at the same time, thus resulting in a somewhat capricious "memory" of the gas-handling system. The observed variations are well established, however, because every sample was measured by at least three independent runs. The error of the published values is estimated to $\pm 1$ unit, but in some cases it might be somewhat larger.

## Investigated Material and Discussion of Results

Salammoniac, $NH_4Cl$, is found in the form of exhalations on active volcanoes in connexion with recent lava flows. The treated samples were collected in the two well-known Italian volcanoes and they were almost pure—the theoretical nitrogen content is 26%. Several hypotheses have been proposed in order to explain the origin and the formation of this nitrogenous mineral.

To the present authors the observation that the ammonium compound is limited to the lower slopes of the volcanoes is most easily explained by assuming that the nitrogen derives from the nitrogen contained in the vegetation and the soil covered by the flow (c.f. Goldschmidt, 1954). No proof seems to have been found that the nitrogen in this case should derive directly from nitrogen coming up from the depths of the crust.

The salammoniac samples form the only well-defined group of the isotope measurements. The reaction leading to the formation of salammoniac does not seem to have been studied from the present aspect and we know nothing about the isotopic constitution of true magmatic nitrogen ("crustal nitrogen"). For these and other reasons it seems impossible to draw any conclusions from the present

results about its formation, but it seems reasonable to assume that this process gives rise to an enrichment of the heavy isotope.

The nitrate samples studied consisted of the nitrate-containing rock, caliche. They were commercial products and were of a rather low purity. The theoretical nitrogen content of sodium nitrate is 16·5%. According to the labels attached typical analyses of the products run (in weight per cent)

| | "Caliche blancho" | "Caliche colorado" |
|---|---|---|
| $NaNO_3$ | 25·00 | 10·00 |
| NaCl | 12·00 | 8·00 |
| $Na_2SO_4$ | 18·00 | 12·00 |
| MgO | 0·80 | 0·40 |
| CaO | 2·00 | 1·20 |
| $K_2O$ | 1·00 | 0·50 |
| Na-borate | 0·90 | 0·70 |
| $KClO_4$ | 0·03 | 0·03 |
| I | 0·04 | 0·04 |

In Table 1 the measurements are marked with I and II. This is an indication of the method of chemical preparation, viz. I indicates that the acid method has been used, II the alkaline Devarda method. It is important to remember this in the present case because the second preparations are not quantitative, the reason being that hydrogen gas was produced so fast that the ammonia in the gas bubbles had not enough time to be completely absorbed by the acid. A similar case for

Table 1. Various samples

| Number | Description of material and locality | N% | $\delta$(N)‰ |
|---|---|---|---|
| 1 | Salammoniac, Vesuvius, 73: 229, lava, Dec. 1868 | 23 | +11·5 |
| 2 | Salammoniac, Etna, Sicily, g4435, eruption 1886 | 23 | +11·0 |
| 3 | Caliche blancho I, 490806, Tocopilla, Chile | 6 | − 2·3 |
| 4 | Caliche blancho II, 490806, Tocopilla, Chile | 4·5 | − 5·0 |
| 5 | Caliche colorado I, 490808, Tocopilla, Chile | 1·2 | − 1·2 |
| 6 | Caliche colorado II, 490808, Tocopilla, Chile | 1·1 | − 5·4 |
| 7 | Air | 76 | 0·0 |
| 8 | *Picea abies*, Ekolsund | 0·044 | − 3·8 |
| 9 | *Betula alba*, Ekolsund, wood | 0·12 | − 2·2 |
| | *Betula alba*, Ekolsund, piece of bark | 0·62 | − 5·0 |

carbon-dioxide absorption has been described by Baertschi (1952). In both cases the light molecules are absorbed preferentially by the sourrounding medium resulting in too small $\delta$ values. In the present case they are about 3–4 units smaller than those obtained by quantitative preparations, thus showing the importance of a high degree of accuracy in every phase of the work. Hence the measurements marked I are the ones to be compared with the other values.

The formation of caliche has been discussed extensively in the literature. The chemical aspects of the principal theories are summarized by Goldschmidt (1954, pp. 449–53). No theory so far presented seems to be able to explain all observations, and the present isotopic measurements are of no help in arriving at such an explanation. On one hand they are very different from the salammoniac values but on the other they are very similar to those found for atmospheric nitrogen and some organic substances. The results indicate also that the $\delta$ values of caliche vary. This is what might be expected because caliche is the result of repeated precipitations and re-solutions.

Two series of coal samples were studied in the present investigation. They had been placed at our disposal by Dr. M. Teichmüller and R. Teichmüller. The carbon isotopes of these samples as well as some others had been reported previously in a paper on the influence of metamorphism on the carbon isotope ratios (Wickman, 1953).

The first series consists of Wealden coal from Northern Germany. The coalification of this region has been studied by M. and R. Teichmüller (1948), and they concluded that the degree of coalification is dependent solely on the intensity of the thermal metamorphism. The flora of the Wealden bogs consisted mainly of

Table 2. Wealden coal from Northern Germany

| Number in Wickman (1953) | Locality | volatile matter % waf* | C% (C + H + O = 100) | $^{12}C/^{13}C$ | N% | $\delta$(N)‰ |
|---|---|---|---|---|---|---|
| 1 | Bohmte (NE Osnabrück) | 9·4 | 93·2 | 90·77 | 0·9 | +2·5 |
| 2 | Core drilling Probsthagen 1646 m | 14·1 | 92·8 | 90·73 | 0·9 | +2·5 |
| 5 | Coal seam 3, Reinsen | 21·7 | 92·2 | 90·75 | 1·2 | +3·5 |
| 10 | Harrl near Bückeberg | 25·8 | 88·3 | 90·98 | 1·7 | +3·5 |
| 14 | Coal seam 4, Strubberg (Teutoburger Wald)† | 30·6 | 78·1 | 90·80 | 1·2 | +2·5 |
| 15 | Coal seam 3, Borgloh (Teutoburger Wald) | 31·2 | 88·3 | 90·81 | 1·2 | +3·0 |
| 23 | Hammerstein (Teutoburger Wald) | 36·4 | 86·2 | 90·72 | 1·0 | +1·5 |
| 28 | Limberg (Teutoburger Wald) | 44·2 | 82·7 | 90·72 | 1·2 | +3·5 |

* After M. and R. Teichmüller; waf = water and ash-free substance:
† Strongly oxidized sample.

gymnosperms, but pteridophytes, especially ferns, also contributed to the formation of peat. The results are shown in Table 2 together with the $C^{12}/C^{12}$ ratios and some chemical data from which an idea of the degree of coalification can be formed.

The second series consists of samples of Carboniferous coal from Rhineland-Westphalia in Western Germany. The coalification of this region has been studied by Böttcher and R. and M. Teichmüller (1949). In this case the important peat-forming plants were pteridophytes, and to some extent gymnosperms and pteridosperms. The results are given in Table 3 together with other useful data.

Air-dried wood samples of birch and fir were studied in order to obtain some idea of the values in living plants. A piece of the bark of the birch sample was also tested because the nitrogen content of bark is higher than that of wood. The results are shown in Table 1.

Table 3. Carboniferous coal from Northwestern Germany

| Number in Wickman (1953) | Locality | % volatile* matter waf | C% (C + H + O = 100) | $^{12}C/^{13}C$ | N% | $\delta$(N)% |
|---|---|---|---|---|---|---|
| 1 | 33 cm coal seam, Laurweg Mine, Aachen | 6·7 | 94·9 | 90·56 | 1·2 | −2·5 |
| 2 | 2. "Riffel" under coal seam "Furth" Maria Mine | 12·6 | 92·8 | 90·54 | 1·3 | 0·0 |
| 9 | Sonnenschein coal seam, Neu-Iserlöhn Mine | 19·1 | 91·2 | 90·67 | 1·4 | −1·0 |
| 13 | Sonnenschein coal seam, Minister Stein | 24·4 | 90·3 | 90·51 | 1·2 | −1·5 |
| 16 | Coal seam C, Fritz-Heinrich Mine | 33·3 | 86·3 | 90·62 | 1·2 | +0·5 |

* After H. Böttcher, M. and R. Teichmüller (1949); waf = water and ash-free substance

This selection of organic substances is by no means complete and the number of samples studied is very small. In spite of these deficiencies the data indicate several groupings. The nitrogen from living matter seems to be somewhat lighter than that from fossil coal. It is of course premature to draw any definite conclusions from the present measurements.

There is also a small difference between the $\delta$ values of the two groups of coal samples. The Wealden-coal nitrogen is heavier than the Carboniferous coal. It is interesting to observe also that the carbon isotopes are grouped around different mean values, but the order is reversed in this case, i.e., the lightest coal

samples are the youngest. The explanation of this difference—if it is real and not just coincidental—must be left to the future.

Within each coal series no effect of metamorphism can be observed on the $\delta$ values. The accuracy of the measurements is too low, however, to make this statement certain. It might be remembered that for the carbon isotopes no such effect could be traced on the same material (Wickman, 1953).

In conclusion it can be said that nitrogen shows small variations in the relative abundance of its isotopes. Of the present materials tested it is only salammoniac that seems to show a definite differentiation in comparison with the other substances. The observed range of variation is 1·5‰, or only less than half of that observed for the stable carbon isotopes.

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## References

Baertschi P. (1952) *Helvetica Chimica Acta* **35,** 1030.
Böttcher H., Teichmüller M., and Teichmüller R. (1949) *Glückauf* **85,** 81.
Goldschmidt V. M. (1954) *Geochemistry*, Oxford.
Hoering T. (1955) *Science* **122,** 1233.
Hutchinson G. E. (1944) *Amer. Scientist* **32,** 178.
Ingerson E. (1953) *Bull. Geol. Soc. Amer.* **64,** 301.
Smith jr. P. V. and Hudson jr. B. E. (1951) *Science* **113,** 577.
Sprinson D. B. and Rittenberg D. (1949) *J. Biol. Chem.* **180,** 707.
Teichmüller M. and Teichmüller R. (1948) *Z. Dtsch. Geol. Ges.* **100,** 498.
White W. C. and Yagoda H. (1950) *Science* **111,** 307.
Wickman F. E. (1953) *Geochim. et Cosmochim. Acta* **3,** 244.

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# Étude photographique de la distribution de la radioactivité dans la granodiorite de l'Adamello

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**Abstract**—The granodiorite from Adamello (Italy) shows a distribution of the α-radioactivity similar to that found in granitic rocks. This distribution is characterized by its heterogeneity. More than 95% of the activity is concentrated in accessories which amount to 0·1% of the volume of the rock. The most active accessories are 100,000 times more active than the essential minerals. In some cases, more than 90% of the α-radioactivity, apparently connected to the essential minerals is in fact due to microscopic inclusions of accessories. The apparent enrichment in uranium and thorium of the ferromagnesian minerals, pointed out by several authors, is due to the abundance of radioactive inclusions in those minerals and not to the substitution by uranium and thorium of certain elements of their crystalline lattice.

Very radioactive inclusions have been found. Their uranium and thorium content exceeds 10%. Their exact identification is not possible, but there are good reasons to believe that the most active are uraninite and torbernite.

Allanite, the most active among the usual accessories, emits 0·47α/cm²/sec. corresponding to an uranium content of 0·16%. Following order of decreasing activity, then come: titanite, zircon, epidote, apatite.

The "real activity" of the essential minerals, quartz, feldspar, biotite, is of the order of $3 \cdot 10^{-5}$ α/cm²/sec which would correspond to an uranium concentration of the order of $10^{-7}$ gr/gr.

In contradiction to what has been observed in other granitic rocks, Adamello's granodiorite does not show any concentration of radioactivity into boundaries between crystals.

Relationships between the intensity of the pleochroic haloes and the activity of the inclusions which produce them are discussed.

## 1. Introduction

Le massif granodioritique de l'Adamello fait l'objet, depuis de nombreuses années, d'études géologiques et pétrographiques aux Instituts de Géologie et de Minéralogie de l'Université de Padoue.

Dans le cadre d'une étude de la distribution de la radioactivité dans les roches éruptives par la méthode photographique (Picciotto, 1950–1951), nous avons cru intéressant d'étudier les faciès les plus typiques de ce massif intrusif si bien connu aux points de vue géologique, pétrographique et chimique.

Le massif de l'Adamello se situe dans les Alpes méridionales, aux confins du Trentin et de la Lombardie. L'intrusion de la masse est certainement post triasique, car elle a métamorphosé les sédiments du Trias. Sur la base de diverses considérations géologiques et pétrographiques, l'intrusion serait postérieure au paroxysme alpin, entre l'éocène supérieur et le miocène inférieur.

Les faciès pétrographiques dominants sont les granodiorites et les tonalites. On retrouve cependant une série de différenciations très variées allant des leucogranites aux gabbros et aux horneblendites.

Pour de plus amples renseignements sur la géologie et la pétrographie du massif de l'Adamello, nons renvoyous aux publications de A. Bianchi et Gb.

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Dal Piaz où on trouvera également une bibliographique complète sur le sujet.

Dans ce travail, nous avons étudié la distribution de la radioactivité dans les faciès granodioritiques qui sont les plus représentatifs de la masse intrusive.

Notre but principal était d'établir la répartition de la radioactivité à l'échelle microscopique entre les différents minéraux et non de mesurer la radioactivité moyenne des divers faciès.

Nous avons utilisé la méthode des émulsions photographiques nucléaires qui se prête particulièrement bien à ce genre d'étude. Pour les principes et la technique de cette méthode, nous renvoyons aux travaux publiés (Baranov et Kretschmer, 1935; Curie, 1946; Hee, 1948; Poole Bremner, 1948; Picciotto, 1949; Coppens, 1950; Buttlar et Houtermans, 1951; Tamburino et Stella, 1952; Imbo et Casertano, 1953; Barbera, Curatelo, Indovina Addario, Palumbo et Santangelo, 1953; Ferretti, Sforzini, Festa et Ippolito, 1954). On trouvera une bibliographie plus complète dans Yagoda (1949) et Rankama (1954). Le présent travail a fait récemment l'objet d'une publication plus détaillée (Hieke-Merlin, Picciotto et Wilgain, 1955).

## 2. Description Pétrographique Sommaire des Faciès Étudiés

Nous avons étudié des roches du groupe du Baïtone, dans l'Adamello nord-occidental; ces roches représentent le faciès acide intermédiaire de tout le massif. L'étude géologique et pétrographique détaillée de la zone du Baïtone a été effectuée par G. Schiavinato (1949).

La granodiorite du Baïtone est à structure holocristalline à grain moyen. Les minéraux leucocrates sont représentés par le quartz, l'orthose et les plagioclases; ces derniers sont les feldspaths dominants et présentent une structure zonaire; leur composition moyenne est celle d'une andésine (40% An). Les éléments ferro-magnésiens sont représentés, dans les faciès les plus acides, par la biotite seule. Dans les termes moins acides vient s'ajouter l'amphibole (hornblende verte).

Parmi les minéraux accessoires, on trouve: le zircon, la magnétite, l'apatite, la titanite et diverses espèces d'épidote: pistachite en cristaux idiomorphes, probablement d'origine primaire, grains de composition intermédiaire entre la clinozoisite et la pistachite liés à la chloritisation de la biotite et enfin orthite brune relativement fréquente en grandes plages.

## 3. Technique des Émulsions Coulées sur Sections Minces

Dans la plupart des travaux antérieurs, la technique utilisée consistait à appliquer une plaque photographique sur une section polie ou transparente ou encore, sur la roche broyée. Cette technique est commode mais ne permet pas d'obtenir le maximum de précision sur la localisation des particules $\alpha$.

Il y a toujours une erreur sur la corrélation entre les surfaces correspondantes de la plaque et de l'échantillon. Une autre source d'imprécision provient de la couche d'air qu'il est impossible d'éviter entre la plaque et l'échantillon. Le parcours des $\alpha$ dans l'air est environ 2.000 fois plus grand que dans les solides. les particules $\alpha$ émises tangentiellement peuvent ainsi accomplir un long trajet dans cette couche d'air avant de rencontrer la surface de l'émulsion.

Ces difficultés peuvent être évitées en utilisant une technique assurant un parfait contact de l'émulsion et de la roche et ne nécessitant pas de séparer l'émulsion pour le développement.

Ces conditions sont remplies, soit en utilisant des feuilles d'émulsion sans support (Stieff et Stern, 1952), soit en coulant une couche d'émulsion liquide sur la section mince (Ford, 1952; Picciotto, 1952). Dans les deux cas, l'émulsion est développée sans la séparer de l'échantillon. On peut observer simultanément au microscope les constituants de la roche et les trajectoires des particules $\alpha$.

Dans le présent travail, nous avons utilisé la technique des émulsions coulées sur les sections minces. Nous pensons utile de donner quelques détails techniques.

*Coulée de l'émulsion*

Les sections minces de 35 $\mu$, non couvertes, sont nettoyées à l'alcool, lavées dans un courant d'eau bidistillée et séchées à l'abri des poussières. Quelques $cm^3$ d'émulsion Ilford C2 "in gel form" sont fondus dans un tube de verre maintenu 10 minutes à 45°C. L'émulsion liquide est versée goutte à goutte sur la section mince, tenue horizontale. Il faut utiliser environ 0,1 $cm^3$ d'émulsion par $cm^2$ pour obtenir une épaisseur de 50 à 100 microns après séchage. La section couverte de l'émulsion est maintenue horizontale dans un dessicateur en présence de silicagel pendant une dizaine d'heures. Il est important que l'émulsion soit sèche dans toute son épaisseur pour éviter l'effacement de l'image latente. Après séchage, les sections ont été conservées pendant 3 mois à 4°C, en atmosphère sèche.

*Développement*

Pour obtenir un développement homogène dans toute l'épaisseur de l'émulsion et pour réduire le gonflement de la gélatine risquant de décoller l'émulsion ainsi que l'action chimique du révélateur sur la roche, nous avons utilisé la méthode de développement àdeux températures (Dilworth, Occhialini et Payne, 1948) avec un révélateur à l'amidol à un pH voisin de la neutralité (Dilworth, Occhialini et Vermaesen, 1950).

Révélateur: Eau: 1.000 g
Sulfite de soude anhydre: 12 g
Amidol: 3 g
Bromure de potassium: 0,5 g
Acide borique: 4 g

La procédure suivante est donnée à titre indicatif; il est nécessaire de faire des essais préliminaires de développement, vu les variations de sensibilité de l'émulsion d'une série à l'autre.

Imprégnation dans l'eau distillée à 4°C: 15 min.
Imprégnation dans le révélateur à 4°C: 40 min.
Le révélateur est jeté et la plaque portée à sec à 14° pendant 40 minutes.
Bain d'arrêt: acide acétique 1% à 4°C pendant 5 min.
Fixage dans l'hyposulfite 30% à 10°C et lavage dans l'eau courante pendant 2 à 3 heures.

*Observation*

L'observation des sections recouvertes d'émulsion a été effectuée avec un microscope polarisant binoculaire à un grossissement de 500 fois. L'usage d'un objectif à immersion est indispensable. Toutes les particules $\alpha$ ayant une trajectoire résiduelle dans l'émulsion supérieure à 5 $\mu$ ont été repérées et reportées sur une photographie agrandie de la section mince.

## 4. Résultats Expérimentaux

Quatre sections minces de granodiorite ont été complètement étudiées; elles correspondent à trois types acides (n° Ad 5, Ad 7 et Ad 8) et un type plus basique (Ad 9) riche en minéraux ferromagnésiens. Cette dernière roche provient d'une

masse lenticulaire d'un mètre de diamètre environ, incluse dans la granodiorite typique. De telles ségrégations basiques de dimensions très variées se présentent souvent dans la masse granodioritique de l'Asamello.

Un certain nombre d'autres sections de granodiorite ont été soumises à un examen plus rapide pour des problèmes spéciaux tels que la recherche d'inclusions très actives ou de halos pléochroïques.

Les résultats détaillés de l'observation microscopique se trouvent dans notre publication déjà citée (1955). A titre d'exemple, nous donnons ici les résultats de l'observation de la section Ad 5 (tableaux 1 et 2). Dans le tableau 3, on trouvera les activités des minéraux dans les quatre sections minces.

Nous avons appelé "activité réelle", l'activité réellement liée à la phase minéralogique, envisagée par opposition à "l'activité totale" qui comprend l'activité

Tableau 1. lame Ad 5

Exposition: 113 jours

| I<br>Minéral | II<br>Nombre d'$\alpha$ | III<br>Surface en $cm^2$ | IV<br>Activité $\alpha/cm^2$. sec | V<br>Répartition min-incl. | VI<br>Activité relative (Feld = 1) | VII<br>U en g/g Th/U = 3 |
|---|---|---|---|---|---|---|
| Section mince | 2600 | 3 | | | | |
| *Quartz* | 1486 | 2,1 | $7{,}2 \cdot 10^{-5}$ | 100 | 1,9 | $0{,}28 \cdot 10^{-6}$ |
| Inclusions | 683 | | | 45 | | |
| Quartz | 803 | | $4{,}1 \cdot 10^{-5}$ | 55 | 1,1 | $0{,}16 \cdot 10^{-6}$ |
| *Feldspath* | 568 | 0,70 | $8{,}4 \cdot 10^{-5}$ | 100 | 2,3 | $0{,}34 \cdot 10^{-6}$ |
| Inclusions | 300 | | | 54 | | |
| Feldspath | 268 | | $3{,}7 \cdot 10^{-5}$ | 46 | 1 | $0{,}15 \cdot 10^{-6}$ |
| *Biotite* | 436 | 0,19 | $23{,}6 \cdot 10^{-5}$ | 100 | 6,3 | $0{,}91 \cdot 10^{-6}$ |
| Inclusions | 281 | | | 63 | | |
| Biotite | 155 | | $8{,}2 \cdot 10^{-5}$ | 37 | 2,2 | $0{,}32 \cdot 10^{-6}$ |
| *Amphibole* | 49 | 0,0033 | $165 \cdot 10^{-5}$ | 100 | 44 | |
| Inclusions | 26 | | | 50 | | |
| Amphibole | 23 | | 82 | 50 | 22 | |
| Orthite | 36000* | 0,0065 | 0,58 | | 16000 | $2{,}9 \cdot 10^{-3}$ |
| Zircon | | | 0,18 | | 4800 | $0{,}54 \cdot 10^{-3}$ |
| Titanite | | | 0,13 | | 3500 | $0{,}49 \cdot 10^{-3}$ |
| Apatite | | | 0,013 | | 350 | $0{,}046 \cdot 10^{-3}$ |
| Interstices | 40 | | | | | |

* L'activité a été une mesurée sur une fraction de la surface (6000 $\alpha$ comptés).

Tableau 2. lame Ad 5

Teneur en volume des minéraux accessoires dans chacun des minéraux essentiels

| Minéral | Apatite | Zircon | Sphène |
|---|---|---|---|
| Quartz | $0{,}3 \cdot 10^{-3}$ | $0{,}06 \cdot 10^{-3}$ | $0{,}01 \cdot 10^{-3}$ |
| Feldspath | $0{,}07 \cdot 10^{-3}$ | $0{,}07 \cdot 10^{-3}$ | $0{,}17 \cdot 10^{-3}$ |
| Biotite | $17 \cdot 10^{-3}$ | $1{,}0 \cdot 10^{-3}$ | $0{,}5 \cdot 10^{-3}$ |
| Amphibole | $50 \cdot 10^{-3}$ | — | — |
| Section mince | $1{,}3 \cdot 10^{-3}$ | $0{,}12 \cdot 10^{-3}$ | $0{,}07 \cdot 10^{-3}$ |

Tableau 3. Activités spécifiques des quatre lames minces en $\alpha/cm^2$. sec

| | | (Ad 5) | (Ad 7) | (Ad 8) | (Ad 9) |
|---|---|---|---|---|---|
| Quartz | réel | $4{,}1 \cdot 10^{-5}$ | $1{,}9 \cdot 10^{-5}$ | $2{,}4 \cdot 10^{-5}$ | |
| | total | $7{,}2 \cdot 10^{-5}$ | $7{,}5 \cdot 10^{-5}$ | $5{,}5 \cdot 10^{-5}$ | |
| Feldspath | réel | $3{,}7 \cdot 10^{-5}$ | $1{,}2 \cdot 10^{-5}$ | $1{,}6 \cdot 10^{-5}$ | $3{,}7 \cdot 10^{-5}$ |
| | total | $8{,}3 \cdot 10^{-5}$ | $6{,}5 \cdot 10^{-5}$ | $5{,}9 \cdot 10^{-5}$ | $39{,}0 \cdot 10^{-5}$ |
| Biotite | réel | $8{,}2 \cdot 10^{-5}$ | $2{,}0 \cdot 10^{-5}$ | $4{,}3 \cdot 10^{-5}$ | |
| | total | $23{,}6 \cdot 10^{-5}$ | $16{,}3 \cdot 10^{-5}$ | $21{,}1 \cdot 10^{-5}$ | $2{,}6 \cdot 10^{-5}$ |
| Amphibole | réel | | | — | $21{,}1 \cdot 10^{-5}$ |
| Orthite | | $0{,}58 \cdot 10^{-5}$ | — | 0,36 | — |
| Titanite | | $13 \cdot 10^{-2}$ | — | — | $11 \cdot 10^{-2}$ |
| Zircon | | $18 \cdot 10^{-2}$ | $6{,}1 \cdot 10^{-2}$ | $11{,}5 \cdot 10^{-2}$ | $9 \cdot 10^{-2}$ |
| Apatite | | $13 \cdot 10^{-3}$ | $14{,}4 \cdot 10^{-3}$ | $8{,}0 \cdot 10^{-3}$ | $8 \cdot 10^{-3}$ |
| Epidote | | — | $48{,}2 \cdot 10^{-3}$ | $58{,}0 \cdot 10^{-3}$ | — |

réelle plus l'activité liée aux inclusions. Comme on l'a déjà souligné (Picciotto, 1950), cette valeur de l'activité réelle est seulement une limite supérieure.

Dans les lames Ad 7 et Ad 8, ainsi que dans d'autres sections, nous avons trouvé des inclusions opaques très petites (5 à 30 $\mu$) dont l'activité spécifique est supérieure à 50 $\alpha/cm^2$ sec.

Les figures 1(a) et 1(b) représentent respectivement la répartition de l'activité entre les différents minéraux et la fraction de volume occupé par chacun de ces

minéraux dans la roche. Ces données ne portent que sur trois sections minces (Ad 5, 7 et 8) et ne prétendent pas représenter des valeurs moyennes significative pour l'ensemble de la granodiorite; néanmoins, elles suffisent à montrer que la grande majorité de l'activité est concentrée dans une très petite fraction du volume total.

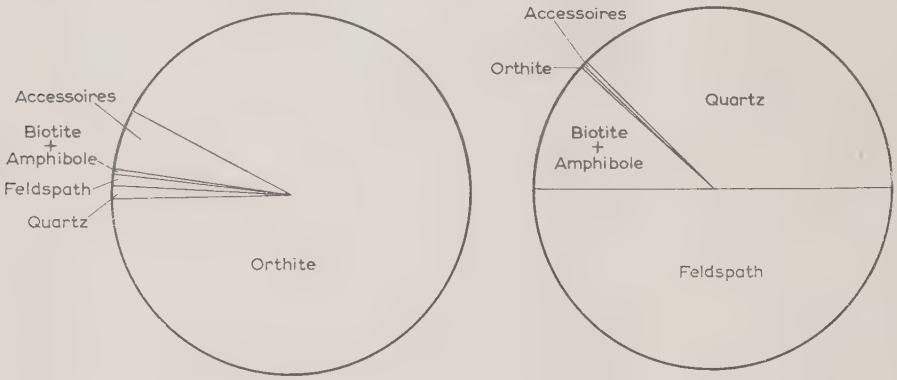


Fig. 1(a). Répartition de l'activité α totale entre les différents minéraux.
Fig. 1(b). Proportion du volume de la roche occupée par les différents minéraux.

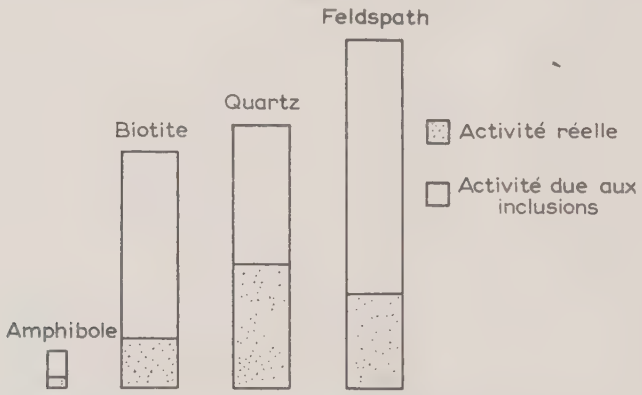


Fig. 2. Répartition de l'activité α liée aux minéraux essentiels entre les inclusions dans ce minéral et le minéral lui-même.

La figure 2 illustre le fait que la majorité de l'activité liée aux minéraux essentiels provient en réalité d'inclusions microscopiques de minéraux accessoires.

La figure 3 représente, à titre d'exemple, la répartition topographique de tous les α émis par une partie de la section Ad 5.

## 5. Discussion des Résultats

(1) *Distribution de l'activité*

L'activité α est distribuée d'une façon très hétérogène, comme dans les roches granitiques précédemment étudiées (Picciotto, 1950).

La majeure partie (plus de 95%) de l'uranium et du thorium de la roche est concentrée dans des minéraux accessoires: minéraux opaques et indéterminables,

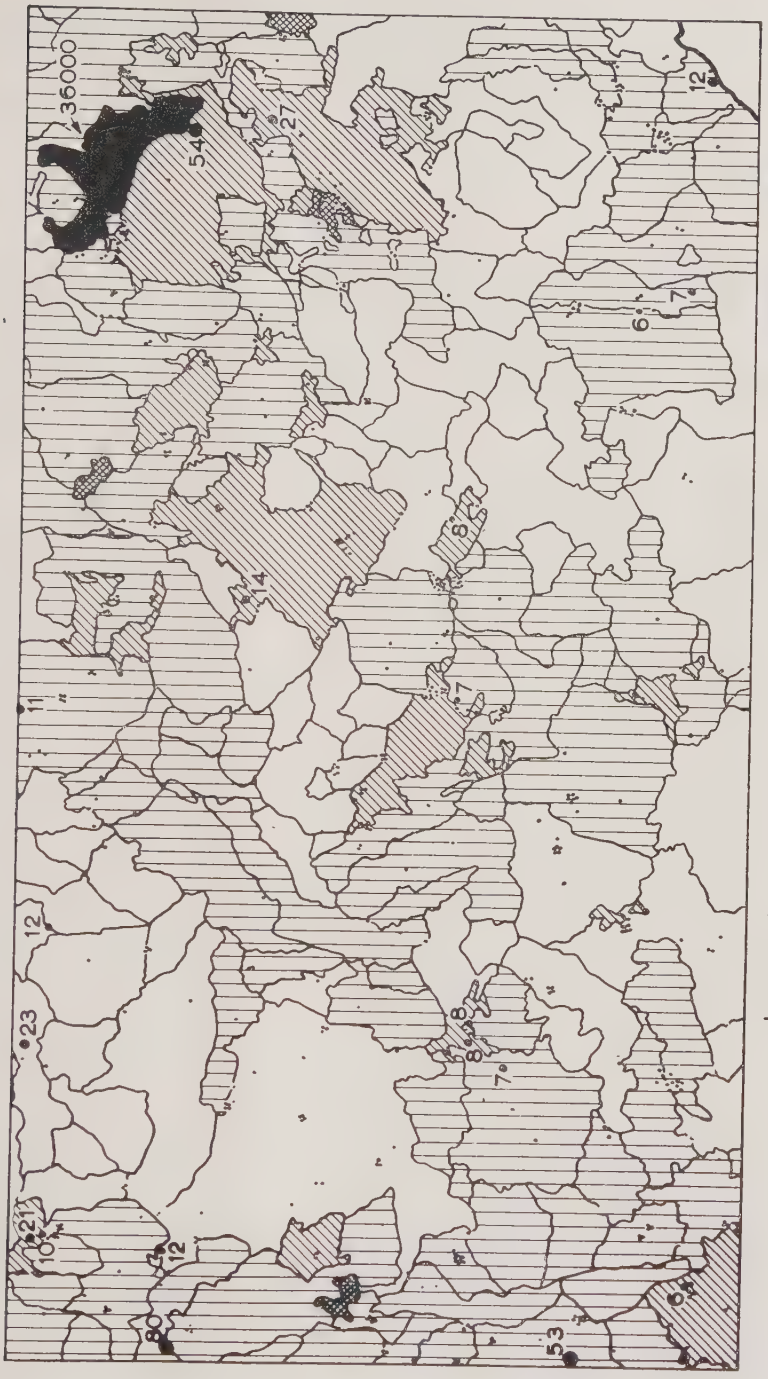


Fig. 3. Distribution des particules α émises par la section mince Ad 5 (exposition 113 jours). Chaque point représente une particule α; les groupes de plus de 5 α sont représentée par des cercles pleins, le nombre d'α étant écrit à côté du cercle.

orthite, titanite, zircon, représentant environ un millième du volume de la roche.

Une fraction considerable (60 à 90%) de l'activité apparemment liée aux minéraux essentiels provient en fait d'inclusions microscopiques de minéraux accessoires.

Les activités spécifiques réelles des divers minéraux présentent des écarts considérables. Les accessoires les plus actifs sont 100.000 fois plus actifs que les minéraux essentiels.

(2) *Activité intersticielle*

Une attention spéciale a été apportée à l'activité éventuellement localisée dans les fissures et interstices entre minéraux; la méthode de coulée utilisée ici est particulièrement adaptée à cette étude qui demande une localisation très précise de l'origine des $\alpha$.

A part son intérêt géochimique, cette question joue un rôle important dans le problème des mesures d'âges par la méthode à l'hélium.

La concentration de l'uranium dans les interstices avait déjà été suggérée par Piggot (1929); elle a été mise en évidence par Hurley (1950) sur le granite de Quincy et par Picciotto (1950) sur le granite du Lac Blanc.

La méthode photographique a permis de démontrer dans le cas du granite du Lac Blanc que 18% de l'activité totale d'une section était concentrée dans les interstices.

Dans les granodiorites de l'Adamello, nous n'avons pas trouvé de concentration d'activité dans les interstices (moins de 1% de l'activité totale).

(3) *Echantillonage pour les mesures de radioactivité*

Le type de distribution d'activité révélée par la méthode photographique confirme ce qui était déjà connu par les méthodes de mesures classiques: qu'il est très difficile d'obtenir un échantillon moyen représentatif de la concentration en uranium et thorium d'une roche acide. Par exemple, dans la section Ad 7, nous avons trouvé plusieurs grains de dimension de l'ordre de quelques microns, représentant moins de un millionième du volume de la roche, mais dont la contribution à l'activité était supérieure à celle de tout le reste de la section.

La méthode photographique peut être très utile pour fixer les dimensions minimum d'un échantillon représentatif de la radioactivité de la roche.

(4) *Concentration en Uranium et Thorium*

L'activité $\alpha$ spécifique dépend des concentrations en U et Th; mais pour obtenir séparément ces deux concentrations, il faut une mesure indépendante du rapport Th/U. Cette mesure peut se faire par le spectre des longueurs des $\alpha$ (Buttlar et Houtermans, 1951; Imbo et Casertano, 1952), mais cette méthode est longue et peu précise. Une autre solution serait de mesurer la concentration en U par comptage des fragments de fission après irradiation aux neutrons (Curie et Faraggi, 1951.

Nous n'avons pas essayé de déterminer séparément U et Th. Pour donner néanmoins un ordre de grandeur, nous avons supposé que le rapport des concentrations en Th et U est égal à 3 qui est proche de la valeur moyenne connue

(Keevil, 1944). Les concentrations en uranium données dans ce travail sont toutes calculées avec cette convention à partir des activités α et n'ont qu'une valeur indicative.

Etant donné la distribution très hétérogène de l'activité, il est impossible de donner une valeur de l'activité moyenne de la roche à partir seulement des 4 sections minces observées.

(5) *Activité des minéraux essentiels*

Le tableau 3 groupe les activités specifiques de tous les minéraux.

Dans la colonne V du tableau 1 et dans la figure 2, on peut voir que 50 à 80% de l'activité des minéraux essentiels est liée aux inclusions. Ce résultat que la méthode photographique a pu mettre en évidence d'une façon quantitative montre que les mesures d'U et Th effectuées sur les minéraux essentiels séparés mécaniquement n'ont pas de signification réelle, car la plupart de ces inclusions sont trop petites pour être séparées de leur minéral hôte.

Un exemple intéressant est donné par la section Ad 9 dans laquelle l'activité totale du feldspath est 6 fois plus grande que l'activité moyenne du feldspath dans les 3 autres échantillons. Un tel fait aurait été interprété comme un enrichissement en U et Th dans le feldspath de ce faciès. La méthode photographique montre au contraire que l'activité "réelle" de ce feldspath n'est pas plus grande mais que l'augmentation de l'activité totale est due à sa plus grande richesse en inclusions, ce qui, du point de vue géochimique, pose le problème d'une façon complètement différente.

Les minéraux essentiels ne montrent pas de variation notable de l'activité réelle dans les 4 échantillons, y compris la concentration basique Ad 9.

Les minéraux essentiels de Ad 5 sont systématiquement plus actifs que dans les autres sections sans raison apparente.

Les activités spécifiques réelles du quartz et du feldspath sont très semblables L'activité "totale" de la biotite est en moyenne 3 fois plus haute que celle du quartz et du feldspath, mais le rapport des activités "réelles" est seulement 1,6, ce qui montre à nouveau que l'activité plus élevée de la biotite déjà notée par Piggot

Tableau 4. Concentrations en U et Th dans les minéraux essentiels (Th/U = 3)

| | | Activité spécifique $\alpha/cm^2$. sec | U · $10^{-6}$ g/g | Th · $10^{-6}$ g/g |
|---|---|---|---|---|
| Quartz | réel | $2{,}8 \cdot 10^{-5}$ | 0,11 | 0,33 |
| | total | $6{,}7 \cdot 10^{-5}$ | 0,26 | 0,78 |
| Feldspath | réel | $2{,}5 \cdot 10^{-5}$ | 0,10 | 0,30 |
| | total | $7{,}0 \cdot 10^{-5}$ | 0,28 | 0,84 |
| Biotite | réel | $4{,}3 \cdot 10^{-5}$ | 0,16 | 0,48 |
| | total | $20{,}0 \cdot 10^{-5}$ | 0,74 | 2,22 |

(1929) n'est pas due à une concentration de U et Th dans son réseau, mais à sa richesse en inclusions (Picciotto, 1950).

Le tableau 4 donne les concentrations en U et Th calculées d'après la moyenne des activités spécifiques et avec l'hypothèse que Th/U = 3; il n'a pas été tenu compte de la section Ad 9.

(6) *Activité des minéraux accessoires*

Les minéraux accessoires montrent des activités similaires dans les 4 échantillons. Nous verrons plus loin que les variations d'activité d'une section à l'autre sont du même ordre que les variations à l'intérieur d'un même cristal.

*Accessoires tres actifs.* Dans plusieurs sections (dont Ad 7), nous avons trouvé des centres microscopiques très actifs ayant émis une centaine à plusieurs milliers de particules $\alpha$.

Il est difficile de donner une valeur exacte des activités et des concentrations correspondantes en U et Th car ces inclusions ont des dimensions de quelques microns, inférieures aux conditions d'émission en couche épaisse.

La détermination optique de la nature de ces inclusions est très difficile car elles sont très petites et souvent opaques, même en couche très mince; nous pouvons les grouper de la manière suivante:

(a) lamelles biréfringentes très actives, d'aspect micacé à relief moyen (supérieur à celui du mica), légèrement pléochroïques passant du jaune au vert-brun. Il s'agit probablement de torbernite.

(b) lamelles opaques à très forte radioactivité, formant des halos pléchroïques intenses quand elles sont dans l'amphibole et la biotite (fig. 4). D'après le rayon du halo, la radioactivité est essentiellement due à la famille de l'uranium. L'activité $\alpha$ correspond à une teneur en U comprise entre 10 et 60%. Ces inclusions pourraient être formées d'uraninite.

Tableau 5. Concentration en U et Th des minéraux accessoires

| | Activité spécifique $\alpha/cm^2$ sec | U g/g | Th g/g |
|---|---|---|---|
| opaque (?) | 50 | 0,10–0.60 | |
| orthite | 0,47 | $1,6 \cdot 10^{-3}$ | $4,8 \cdot 10^{-3}$ |
| titanite | 0,11 | $0,42 \cdot 10^{-3}$ | $1,3 \cdot 10^{-3}$ |
| zircon | 0,11 | $0,36 \cdot 10^{-3}$ | $1,1 \cdot 10^{-3}$ |
| épidote | 0,052 | $0,17 \cdot 10^{-3}$ | $0,51 \cdot 10^{-3}$ |
| apatite | 0,011 | $0,04 \cdot 10^{-3}$ | $0,12 \cdot 10^{-3}$ |

(c) Grains très petits, biréfringents à fort relief, ressemblant au zircon et que nous identifions provisoirement avec du xénotime.

Fig. 4(a). Lamelle microscopique opaque, probablement d'uraninite, incluse dans une amphibole et entourée d'un intense halo pléochroïque.

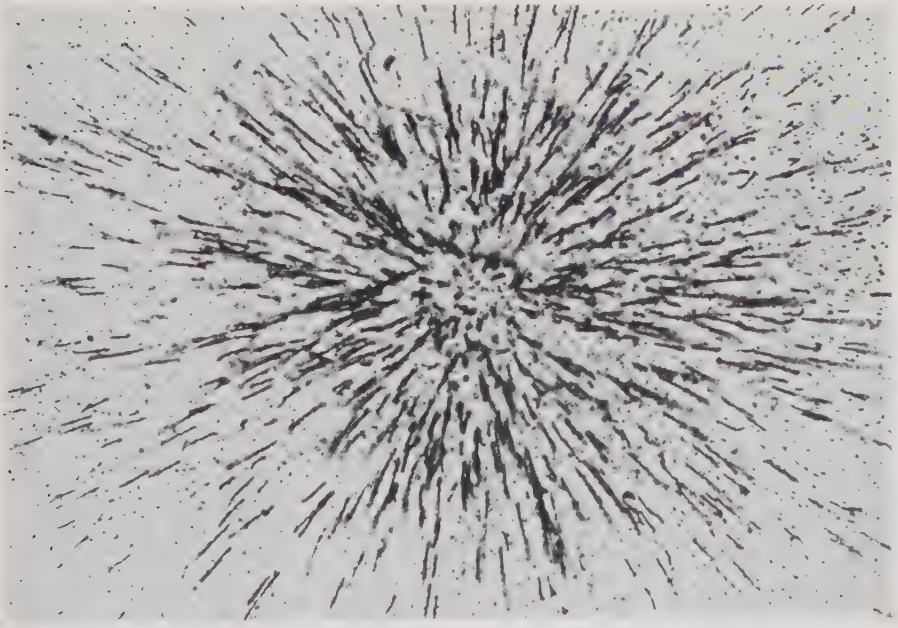

Fig. 4(b). Particules α émises par l'inclusion en 113 jours d'exposition.

Fig. 5(a). Petit cristal d'épidote zoné avec noyau d'orthite.

Fig. 5(b). Trajectoires d'α montrant que seule la zone centrale est active.

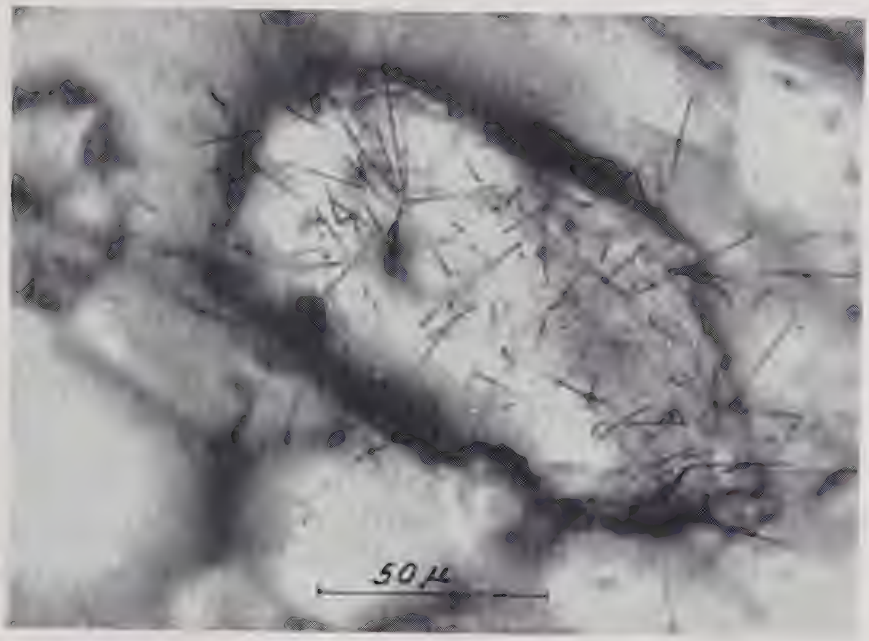


Fig. 6. Cristal de zircon montrant une zone nettement plus active que le reste du cristal.

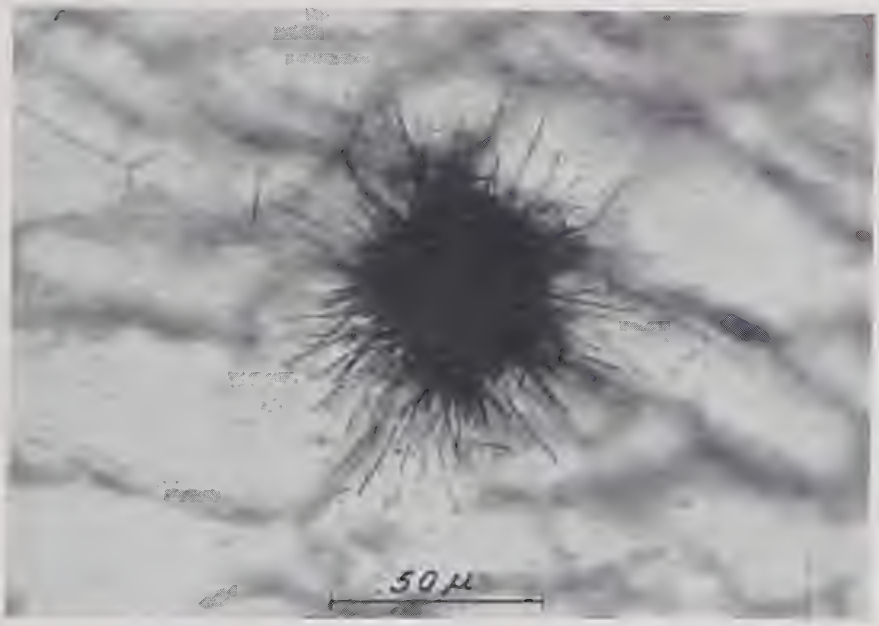


Fig. 7. Trajectoires d'α émises par une inclusion microscopique de torbernite (?) dans le feldspath.

Pour les autres accessoires, l'activité a été mesurée dans des conditions d'émission en couche épaisse, c'est-à-dire seulement sur des cristaux ayant une épaisseur de 35 $\mu$ et des dimensions linéaires supérieures à 50 $\mu$.

Par ordre d'activité décroissante, les accessoires actifs sont: les opaques (uraninite), l'orthite, la titanite, le zircon, l'épidote, l'apatite. Leur concentration moyenne en U, toujours calculée sur la base Th/U = 3 est donnée au tableau 5.

*Comparaison avec d'autres résultats connus*

Les données sur la répartition de l'Uranium et du Thorium dans les roches sont encore peu nombreuses. La comparaison des résultats est rendue difficile par la diversité des méthodes de mesure utilisées.

Le tableau 6 montre la comparaison des activités spécifiques "réelles" des minéraux de l'Adamello avec ceux des deux autres granites précédemment étudies par la même méthode. (Picciotto, 1950). On voit que les activités, tant des minéraux essentiels que des accessoires, sont plus basses dans la granodiorite (à l'exception du quartz du granite du Lac Blanc qui montre une activité exceptionnellement basse).

Parmi les travaux sur la teneur en U et Th de minéraux séparés mécaniquement, les plus importants sont ceux de Keevil et ses collobarateurs (1938, 1942, 1944)

Tableau 6. Comparaison des activités spécifiques dans la granodiorite de l'Adamello et dans 2 granites. Les chiffres supérieurs sont les activités en $\alpha/cm^2$ sec, les chiffres entre parenthèses sont les concentrations en U, toujours avec l'hypothèse Th/U = 3.

| | granite Elbe | granite Lac Blanc | granodiorite Adamello (moyenne de ce travail) |
|---|---|---|---|
| Quartz | $45 \cdot 10^{-5}$ ($1{,}9 \cdot 10^{-6}$) | $1{,}6 \cdot 10^{-5}$ ($6{,}5 \cdot 10^{-8}$) | $2{,}8 \cdot 10^{-5}$ ($1{,}1 \cdot 10^{-7}$) |
| Feldspath | $1 \cdot 10^{-4}$ ($4 \cdot 10^{-7}$) | $2{,}5 \cdot 10^{-4}$ ($1 \cdot 10^{-6}$) | $2{,}5 \cdot 10^{-5}$ ($1 \cdot 10^{-7}$) |
| Biotite | $8{,}4 \cdot 10^{-5}$ ($3{,}0 \cdot 10^{-6}$) | $1{,}7 \cdot 10^{-4}$ ($6{,}1 \cdot 10^{-6}$) | $4{,}3 \cdot 10^{-5}$ ($1{,}7 \cdot 10^{-7}$) |
| Zircon | | 8 ($2{,}4 \cdot 10^{-2}$) | 0,11 ($4{,}2 \cdot 10^{-4}$) |
| Titanite | 9,2 ($3{,}5 \cdot 10^{-2}$) | | 0,12 ($4{,}2 \cdot 10^{-4}$) |
| Apatite | | 0,01* ($0{,}34 \cdot 10^{-4}$) | 0,011 ($4 \cdot 10^{-5}$) |

* Nouvelle valeur mesurée avec plus de précision sur un plus grand nombre de plages d'apatite.

et ceux du groupe de E. S. Larsen (1942, 1952, 1953, 1954). Les roches les plus étudiés sont des granites. Deux exemples deroches granodioritiques complètement étudiées sont la tonalite de Lakeview, Californie (Larsen et Keevil, 1942) et la diorite de Woodson, Californie (Larsen et Phair, 1954).

Les concentrations en U dans les minéraux essentiels et notamment la biotite sont probablement trop élevées dans Lakeview et Woodson à cause de la présence d'inclusions actives inséparables par les moyens mécaniques utilisés.

Le tableau 7 donne la comparaison des teneurs en uranium dans la granodiorite de l'Adamello, la tonalite de Lakeview et la granodiorite de Woodson. Le rapport Th/U dans la tonalite de Lakeview est très voisin de 3 pour tous les minéraux. Le Th n'a pas été mesuré dans la granodiorite de Woodson.

Tableau 7. Concentrations en uranium en grammes par tonne dans trois roches granodiotitiques

| | Adamello | Lakeview | Woodson |
|---|---|---|---|
| Quartz | 0,11 (total 0,26) | 0,3 | 2,2 |
| Feldspath | 0,10 (total 0,28) | 0,3 | 8,2(perthite) 6,0(plagiocl.) |
| Biotite | 0,16 | 1 | 2,6 |
| Amphibole | (total 0,74) | | 2,8 |
| Otrhite | 1600 | | |
| Titanite | 420 | 403 | |
| Zircon | 360 | 611 | 1750 |
| Apatite | 40 | 85 | 62 |
| Monazite | | | 820 |
| Xénotime | | | 12700 |

*Variations de l'activité dans des cristaux individuels*

Des variations de la teneur en uranium et thorium dans des monocristaux de grande taille de zircon ou d'autres minéraux ont déjà été mises en évidence par diverses méthodes, voir par exemple (Buttlar et Houtermans, 1951) et (Larsen, Waring et Berman, 1953).

Un des avantages de la méthode photographique est de pouvoir étudier les variations de la radioactivité dans des cristaux de petite taille. Nous avons, à titre d'exemple, étudié les variations de l'activité dans un cristal d'orthite de la section Ad 5. Le cristal a été divisé en 45 zones délimitées par des clivages. Dans chaque zone, on a compté de 100 à 200 $\alpha$ en vérifiant l'épaisseur et l'homogénéite

du cristal; on a évité de compter les régions proches des bords du cristal ou des fractures. Aucune variation d'activité n'a d'ailleurs été constatée dans les fractures. La perte d'émanation semble très faible, car nous n'avons pas trouvé d'étoiles à 3 branches dues au thoron ou au radon qui auraient diffusé dans l'émulsion.

La répartition n'est pas homogène. L'activité moyenne est de 0,58 $\alpha/cm^2$ sec, les zones les plus actives atteignent $1\alpha/cm^2$ sec et les moins actives 0,2. Les écarts à la moyenne ne sont pas considérables, mais dépassent largement les fluctuations statistiques.

Un autre exemple de distribution non homogène de l'activité est donné par la figure 5 qui représente un cristal d'épidote à structure zonaire; seule la zone centrale montrant les caractères de l'orthite, est radioactive.

Cette question de l'homogénéité de distribution des éléments radioactifs dans les minéraux présente une grande importance dans les problèmes de mesure d'âge sur minéraux séparés.

*Observations sur les halos pléochroïques*

On sait que les halos pléochroïques autour de certaines inclusions sont un effet de radiation dû aux particules $\alpha$ émises par ces inclusions.

L'intensité d'un halo est fonction, entre autres choses, du nombre total de particules $\alpha$ émises depuis la formation de la roche; c'est donc une fonction de l'âge de la roche ou, plus exactement, de l'âge du minéral dans lequel le halo s'est développé.

Les halos pléochroïques sont, d'autre part, affectés par les conditions physico-chimiques, notamment par la température.

Une étude quantitative des halos pourrait donc fournir des informations intéressantes sur l'âge et l'histoire géologique d'une roche. Une telle étude implique la mesure, d'une part, de l'intensité du halo pléochroïque, d'autre part, de l'activité $\alpha$ de l'inclusion. Cette activité est très faible, de l'ordre de quelques $\alpha$ par jour ou par semaine, vu la petite taille des inclusions. Avant la mise au point des émulsions photographiques nucléaires, il était impossible de mesurer de si faibles activités, aussi les études sur les halos pléochroïques ont surtout porté sur les mesures du diamètre des anneaux (Henderson, 1934, 1939).

La méthode photographique, en permettant la mesure de l'activité des inclusions a ouvert de nouvelles et intéressantes possibilités dans l'étude quantitative des halos.

Coppens (1950) a mesuré l'activité d'inclusions à halo. Le premier essai de corrélation entre l'activité des inclusions et l'intensité des halos en vue de mesure d'âge semble être dû à Hayase (1954). Le paramètre choisi par Hayase, pour définir l'intensité du halo est le "rayon" du halo. Deutsch, Hirschberg et Picciotto (1955) ont étudié les relations entre l'activité de l'inclusion et l'intensité du halo dans diverses roches d'âge connu, l'intensité du halo étant définie par la densité optique moyenne mesurée au microphotomètre. Les observations reproduites ici sont en grande partie tirées de ce dernier travail. Une description détaillée des techniques et une discussion générale seront publiées ailleurs.

Nous nous sommes uniquement intéressés aux *halos dans les biotites* autour d'inclusions de dimensions linéaires supérieures à 50 $\mu$. Les valeurs des activités $\alpha$ correspondent donc à des conditions d'émission en couche épaisse.

Dans ces conditions, les particules $\alpha$ sortant de l'inclusion présentent un spectre d'énergie et de longueur variant d'une façon continue depuis zéro jusqu'au parcours de l'$\alpha$ le plus long (ThC′ = 42 $\mu$ pour la famille du Th, RaC′ = 34 $\mu$ pour la famille de l'U). Les halos ne présentent donc pas une structure en anneaux concentriques, comme dans le cas d'inclusions très petites, mais un effet continu depuis l'inclusion jusqu'a une distance $r$ que nous appelons ici le "rayon" du halo.

*Apatites*

L'activité moyenne des apatites est de $(1{,}1 \pm 0{,}1)\ 10^{-2} \alpha/\text{cm}^2$ sec ($4 \cdot 10^{-5}$ g U/g). Il n'y a jamais de halo observable autour des apatites.

*Zircons*

Dans les lames Ad 5, 7, 8 et 9, l'activité moyenne des zircons est de 0,11 $\alpha/\text{cm}^2$ sec, nous n'avons pu trouver de zircons dans la biotite.

La lame Ad 122, par contre, a fourni les observations suivantes: Il y a 2 groupes de minéraux accessoires développant des halos pléochroïques dans la biotite; ils présentent tous deux des caractères très similaires au zircon mai sont des activités différentes. La petite taille et le faible nombre des inclusions ne nous ont pas permis de vérifier s'il s'agit d'espèces minérales différentes.

Dans le groupe I, l'activité est de l'ordre de 0,1 $\alpha/\text{cm}^2$ sec; ces inclusions sont entourées d'un halo faible dont le rayon est de 14 $\mu$.

Les zircons du groupe II ont une activité de 2,5 $\alpha/\text{cm}^2$ sec et sont entourés de halos intenses et plus étendus de rayon égal à 30 $\mu$.

*Opaque tres actif*

Un des accessoires très actifs signalés au chapitre précédent a été trouvé entre un cristal d'amphibole et un cristal de biotite (Fig. 4). Dans ces deux minéraux, il a développé un halo très intense, dont le noircissement est uniforme, indépendant de la distance à l'inclusion, ce qui indique un effet de saturation dans la coloration. Le rayon de ce halo est de 32 $\mu$ qui correspond au parcours du RaC′, le plus long de la famille de l'uranium. Vu sa très forte intensité, il est probable que ce halo a atteint son rayon maximum.

Nous ne pouvons donner qu'une valeur très approximative de l'activité specifique de cette inclusion car les conditions d'émission en couche infiniment épaisse ne sont pas observées, ses dimensions étant de l'ordre de 10 $\mu$. Nous avons estimé à 50 $\alpha/\text{cm}^2$ sec, l'activité qu'aurait cette inclusion si elle était en couche épaisse.

Ces observations sur les halos sont rassemblées dans le tableau 8 où nous donnons aussi le nombre d'$\alpha$ total émis par cm² en supposant que la roche a un âge de $40 \cdot 10^6$ ans.

Ces conclusions sont en bon accord avec les observations de Hayase (1954) et de Deutsch, Hirschberg et Picciotto (1955). Nous renvoyons à ce dernier travail pour une discussion plus détaillée. On y verra aussi que les points expérimentaux sont encore trop peu nombreux pour en tirer des conclusions sur l'âge, de l'Adamello, sinon que ces roches sont post-carbonifères et plus jeunes que $100 \cdot 10^6$ ans.

## Conclusions

La granodiorite du massif de l'Adamello montre une distribution de la radioactivité $\alpha$ due aux familles du thorium et de l'uranium analogue à celle qui a déjà été mise en évidence dans des roches granitiques, soit par la méthode photographique, soit par d'autres méthodes. Cette distribution est caractérisée par son hétérogénéité, la majeure partie de l'activité est concentrée dans des minéraux accessoires représentant environ 0,1% du volume de la roche. Les accessoires les plus actifs peuvent être 100.000 fois plus actifs que les minéraux essentiels. Plus de la moitié et quelquefois plus de 90% de la radioactivité $\alpha$ apparemment liée

Tableau 8. Halos pléochroïques et activités des inclusions

| Nature de l'inclusion | Activité de l'inclusion en couche épaisse | Nombre total d'$\alpha$ émis en $40 \cdot 10^6$ ans | Aspect du halo | Rayon du halo |
|---|---|---|---|---|
| Apatite | $1{,}1 \cdot 10^{-2}$ $\alpha$/cm$^2$ sec | $1{,}4 \cdot 10^{13}$ $\alpha$/cm$^2$ | pas de halo | $r = 0\ \mu$ |
| Zircon I | $0{,}1 \cdot 10^{-2}$ $\alpha$/cm$^2$ sec | $1{,}3 \cdot 10^{14}$ $\alpha$/cm$^2$ | halo léger | $r = 15\ \mu$ |
| Zircon II | $2{,}5 \cdot 10^{-2}$ $\alpha$/cm$^2$ sec | $3{,}2 \cdot 10^{15}$ $\alpha$/cm$^2$ | halo intense | $r = 30\ \mu$ |
| Opaque (uraninite?) | $50 \cdot 10^{-2}$ $\alpha$/cm$^2$ sec | $6 \cdot 10^{16}$ $\alpha$/cm$^2$ | halo saturé | $r = 32\ \mu$ |

aux minéraux essentiels est en fait due aux inclusions microscopiques d'accessoires actifs. L'enrichissement apparent en uranium et thorium des minéraux ferromagnésiens, mis en évidence par plusieurs auteurs, est due à la plus grande richesse de ces minéraux en inclusions radioactives et non à la substitution par l'uranium et le thorium de certains éléments de leur réseau cristallin.

Parmi les minéraux accessoires, on trouve, en très faible proportion dans la roche, des inclusions microscopiques très radioactives. Leur teneur en uranium ou thorium dépasse 10%, leur identification précise n'est pas possible, mais il y a de bonnes raisons de croire que les plus actives sont de l'*uraninite* (oxyde d'uranium) et de la *torbernite* (phosphate de cuivre et d'uranium).

Parmi les minéraux accessoires plus fréquents, le plus actif est l'orthite qui émet 0,47 $\alpha$/cm$^2$ sec, correspondant à une teneur en uranium de 0,16%. Viennent ensuite, par ordre d'activité décroissante: la titanite, le zircon, l'épidote et l'apatite.

L'activité "réelle" des minéraux essentiels: quartz, feldspath, biotite est de l'ordre de $3 \cdot 10^{-5}$ $\alpha$/cm$^2$ sec, ce qui correspondrait à une concentration en uranium de l'ordre de $10^{-7}$ g U/g.

Contrairement à ce qui a été observé dans d'autres roches granitiques, la granodiorite de l'Adamello ne montre pas de concentration de la radioactivité dans les interstices.

La technique des émulsions coulées sur section mince se prête extrêmement bien à l'étude de la répartition de la radioactivité dans les roches; elle permet

d'exploiter au maximum les avantages de la méthode des émulsions nucléaires: localisation et sensibilité. Il faut cependant souligner les limites de cette méthode, telle qu'elle a été utilisée dans ce travail. Elle n'est ni meilleure ni moins bonne que les méthodes classiques de mesure d'uranium et de thorium, son domaine d'application est différent et on doit la concevoir comme un complément des autres méthodes.

La méthode photographique pour la mesure de l'activité $\alpha$ de sources solides n'est pas très précise. Elle se prête mal à la mesure séparée du thorium et de l'uranium ou à la détermination du rapport thorium-uranium. Elle permet difficilement d'obtenir des valeurs significatives de l'activité ou des teneurs *moyennes* en uranium et thorium d'une roche, on ne peut compter sur elle pour étudier quantitativement les relations d'équilibre radioactif entre les divers émetteurs présents. On sait que les facteurs de ces limitations sont notamment la diffusion des gaz radioactifs; radon et thoron, l'imprécision sur le pouvoir d'arrêt de l'échantillon pour les $\alpha$, l'incertitude statistique sur le nombre de désintégrations comptées.

Par contre cette méthode permet d'obtenir des informations qu'aucune autre méthode ne peut donner, nous avons essayé de démontrer son efficacité dans des problèmes tels que: variation de la radioactivité dans des monocristaux, localisation dans les interstices, discrimination entre la radioactivité réelle et celle qui est due aux inclusions microscopiques, étude préliminaire aux mesures d'âge sur inclusions radioactives, étude quantitative des halos pléochroïques.

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## Bibliographie

Barbera L., Curatolo M., Indovina Addario M. M., Palumbo D., et Santangelo M. (1953) Radioattività di una lava etnea. Studio quantitativo. *Ann. Geofis. Ital.* **VI,** n° 2, 161–172.

Baranov V. I. et Kretschmer S. I. (1935) Utilisation des plaques à couche épaisse pour la recherche de la répartition des éléments radioactifs dans les objets naturels. *Compt. Rend. Acad. Sci. U.R.S.S.* **1,** 543–549.

Bianchi A. et Dal Piaz Gb. (1937) Il settore meridionale del Massiccio dell'Adamello. Relazione sul relivamento e studi preliminari della zona compresa fra la Valle di Stabro e l'Alta Valle del Caffaro. *Bull. Uff. Geol. Ital. Roma* **LXII,** 1–87.

Bianchi A. et Dal Piaz Gb. (1940) Il settore occidentale del Massiccio dell'Adamello. Relazione preliminare sul rilevamento e sugli studi geologicopetrografici compiuti durante l'anno 1939 nell'Alta Val Camonica. *Bull. Uff. Geol. Ital., Roma* **LXV,** 1—18.

Bianchi A. et Dal Piaz Gb. (1948) Differenziazioni petrografiche e metamorfismi selettivi di contatto nel Massiccio dell'Adamello. *Rend. Soc. Miner. Ital.* **V,** Pavia, 1–26.

Bianchi A. et Dal Piaz Gb. (1950) il problema dell'età del Corno Alto nel Massiccio dell'Adamello. *Memorie degli Instituti di Geologia e Mineralogia Univ. Padova* vol. **XVII.**

Buttlar H. V. et Houtermans F. G. (1951) Photographische Messung des U- und Th- Gehaltes nach der Auflagemethode. *Geochim. et Cosmochim. Acta* **2,** 43–61.

Coppens R. (1950) Sur l'emploi de l'émulsion photographique pour la détermination de la radioactivité des roches par l'examen des trajectoires des rayons α. *J. Phys. Radium* **11,** 21–32.

Coppens R. (1950) Sur l'activité des petits cristaux à halo pléochroïque contenus dans un granite. *Compt. Rend.* **231,** 343–345.

Curie I. (1946) Sur la possibilité d'étudier la radioactivité des roches par l'observation des trajectoires des rayons α dans l'émulsion photographique. *J. Phys. Radium* **VII,** 313–319.

Curie I. et Faraggi H. (1951) Autoradiographie par neutrons. Dosage séparé de l'uranium et du thorium dans les minéraux. *Compt. Rend.* **232,** 959–961.

Deutsch S., Hirschberg D., et Picciotto E. (1955) Mesure des âges géologiques par les halos pléochroïques. *Experientia* **11,** 172–178.

Dilworth C., Occhialini G., et Payne R. (1948) Processing thick emulsion for nuclear research. *Nature* **162,** 102–103.

Dilworth C., Occhialini G., et Vermaesen L. (1950) On processing nuclear emulsion. Part I. *Bull. C. Phys. Nucl. Univ. Bruxelles* n° 13a.

Ferretti Sforzini M., Festa C., et Ippolito F. (1954) Sulla applicazione del metodo delle emulsioni nucleari allo studio della radioattività delle lave vesivuane. *Ann. Geofis. Ital.* **VII,** 539-546.

Ford I. H. (1951) Radioactivity of rocks. An improvement in the photographic technique. *Nature* **167,** 273–274.

Hayase I. (1954) Relative geologic age measurements on granites by pleochroic haloes and the radioactivity of the mineral in their nuclei. *Amer. Mineral.* **39,** 761–772.

Hee A. (1948) Recherches sur la radioactivité d'un granite des Vosges par la méthode photographique. *Ann. Geophys.* **4,** 242–252.

Henderson G. H. (1934) A new method of determining the age of certain minerals. *Proc. Roy. Soc.* **A1, 45,** 591–598.

Henderson G. H. (1939) A quantitative study of pleochroic haloes. V. The genesis of haloes. *Proc. Roy. Soc.* **A1, 73,** 250–264.

Hieke Merlin O., Picciotto E., et Wilgain S. (1955) Studio sulla distribuzione della radioattivita nella granodiorite dell'Adamello. *Memorie degli Instituti di Geologia e Mineralogia Univ. Padova, vol.* **XIX,** *Padova.*

Hurley P. (1950) Distribution of radioactivity in granites and possible relation to helium age measurement. *Bull. Geol. Soc. Amer.* **61,** 1–7.

Imbo G. et Casertano L. (1952) Deduzione delle concentrazioni di Uranio e Torio nelle sostanze radioattive con il metodo fotografico. *Ann. Geofis. Ital.* **V,** n° 1, 1–12.

Imbo G. et Casertano L. (1953) Analisi radioattiva delle rocce col metodo fotografico. *Ann. Geofis. Ital.* **VI,** n° 3. 3315–320

Keevil N. B. (1938) The distribution of helium and radioactivity in rocks. I. Mineral separates from the Quincy granite. *Amer. J. Sci.* **36,** 406–416.

Keevil N. B. (1942) The distribution of helium and radioactivity in rocks. II. Mineral separates from the Cape Ann granite. *Amer. J. Sci.* **240,** 13–21.

Keevil N. B. (1944) Thorium-uranium ratios in rocks and minerals. *Amer. J. Sci.* **242,** 309–321.

Keevil N. B., Larsen E. S., et Wank F. J. (1944) The distribution of helium and radioactivity in rocks. VI. The Ayer granite migmatite at Chelmsford, Mass. *Amer. J. Sci.* **242,** 345–353.

Larsen E. S. et Keevil N. B. (1942) The distribution of helium and radioactivity in rocks. III, Radioactivity and petrography of some California intrusives. *Amer. J. Sci.* **240,** 204–215.

Larsen E. S., Keevil N. B., et Harrison H. C. (1952) Method for determining the age of igneous rocks using the accessory minerals. *Bull. Geoll. Soc. Amer.* **63,** 1045–1052.

Larsen E. S., Waring C. L., et Berman J. (1953) Zoned zircon from Oklahoma. *Amer. Mineral.* **38,** 1118–1125.

Larsen E. S. et Phair G. (1954) The distribution of uranium and thorium in igneous rocks. In *Nuclear Geology*, John Wiley and Sons, Inc., New York.

Picciotto E. (1949) L'étude de la radioactivité des roches par la méthode photographique. *Bull. Soc. Belge Géol., Paléontol. et Hydrol.* **58,** 75–90.

Picciotto E. (1950) Distribution de la radioactivité dans les roches éruptives. *Bull. Soc. Belge Geol., Paleontol. et Hydrol.* **59,** 170–198.

Picciotto E. (1952) Utilisation des émulsions liquides dans l'étude de la radioactivité des roches *Bull. C. Phys. Nucl. Univ. Bruxelles* n° 33.

Piggot C. (1929) Radium in rocks: the radium content of some representative granites of the eastern seaboard of the United States. *Amer. J. Sci.* **17,** 13–34.

Poole J. H. J. et Bremner J. W. (1949) Investigation of the distribution of the radioactive elements in rocks by the photographic method. *Nature* **163,** 130–131.

Rankama K. (1954) *Isotope Geology* London, Pergamon Press Ltd.

Schiavinato G. (1951) Relazione sul relivamento geologico-petrografico del gruppo del Baïtone (Adamello nord-occidentale). *Rend. Soc. Miner. Ital.* **VII,** *Pavia.*

Stieff L. R. et Stern T. N. (1952) Preparation of nuclear track plates and stripping films for the study of radioactive minerals. *Amer. Mineral.* **37,** 184–196.

Tamburino S. et Stella A. (1952) Determinazione della radioattività di una pegmatite di Delianova mediante emulsioni nucleari esposte a strati di zoccia polverizzata e compressa ed a sezioni settili. *Notizie di Mineralogia Siciliana e Calabrese, fasc.* **IV.**

Yagoda H. (1949) *Radioactive measurements with nuclear emulsions* John Wiley and Sons, Inc., New York.

Geochimica et Cosmochimica Acta, 1957, Vol. 11, pp. 189 to 193. Pergamon Press Ltd., London

# Comparison of the isotopic abundance of $U^{235}$ and $U^{238}$ and the radium activity ratios in Colorado Plateau uranium ores*

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**Abstract**—The isotopic abundances of uranium and the radium activity ratios of eleven samples of uranium ore from the Colorado Plateau have been measured. No significant variation in the isotopic abundance of the uranium was noted; within the experimental error, the average $U^{235}/U^{238}$ ratio is 137·7. There is a significant variation in the $Ra^{226}/Ra^{223}$ activity ratios (0·048–0·143), which indicates a relatively recent alteration of the ore samples. The variations do not, however, explain the lead-uranium and lead-lead age discrepancies.

Both the published and the unpublished data on the natural variations in isotopic abundance of $U^{235}$ and $U^{238}$ in different geologic materials are limited (Nier, 1939a and b; Inghram, private communication). Although Inghram showed that there were no significant variations in the $U^{235}/U^{238}$ abundance ratio greater than 0·03% (Katz and Rabinowitch, 1951), the possibility has been suggested that the observed variation in the $Ra^{223}/Ra^{226}$ activity ratios and the discrepancies between the $Pb^{206}/U^{238}$ and $Pb^{207}/Pb^{206}$ ages may be due, at least in part, to variations in the $U^{235}/U^{238}$ ratio (Kuroda, 1955). For this reason the $U^{235}/U^{238}$ ratios of eleven samples from a selected group of uranium deposits of the Colorado Plateau area and uranium ores from two other areas have been isotopically analysed. These samples represent a wide variety of uranium ore types. $Ra^{223}/Ra^{226}$ ratios have been determined by Kuroda on many of these samples and $Pb^{206}/U^{238}$ and $Pb^{207}/Pb^{206}$ ages have been determined by Stieff and others (1953) on the same samples or similar materials from the same mines. We are indebted to personnel of the Mass Assay Laboratory of Union Carbide Nuclear Company, Y-12 Plant at Oak Ridge, Tennessee, for the uranium isotope analyses. This study is part of a programme being conducted by the U.S. Geological Survey on behalf of the Division of Research of the U.S. Atomic Energy Commission.

The uranium was completely extracted from the specimens and a minimum of four separate conversions of $U_3O_8$ to $UF_6$ and mass-spectrographic determinations were made on each. All the results were compared with those of the Oak Ridge National Laboratory "N" Standard (0·7115 wt. per cent $U^{235}$). The expressed error is the limit of error of the mean in the 95-per cent confidence level. The results shown in Table 1 are for eleven ore specimens from mines on or near the Colorado Plateau. The isotopic data for samples of pitchblende from Great Bear Lake and Joachimsthal are shown for comparison. The following geologic information concerning these specimens is known:

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Samples G, J, S, and N are from a series of samples from a channel sample collected from the Mineral Joe mine, Montrose County, Colorado, and are fully described by Garrels and others (in preparation). The mine is in the Morrison formation of Jurassic age. The channel was cut across a mineralized zone which graded from black, partially oxidized-uranium ore, through oxidized yellow-brown ores, into unmineralized rock. Sample N is partially oxidized ore. J is yellow-brown

Table 1. Comparison of the radium-activity ratios and the uranium isotope abundances in samples from the Colorado Plateau

| Sample No. | Location and description | Activity ratio $\frac{N_{Ra^{223}}\lambda_{Ra^{223}}}{N_{Ra^{226}}\lambda_{Ra^{226}}}$ | Weight per cent $U^{235}$ | $N_{U^{238}}/N_{U^{235}}$ |
|---|---|---|---|---|
| G | Heavily oxidized uranium ore, Mineral Joe mine, Colo. | —* | 0·7147 ± 0·0025 | 137·1 ± 0·35 |
| S | Oxidized ore, composite sample, Mineral Joe mine, Colo. | —* | 0·7121 ± 0·0033 | 137·7 ± 0·64 |
| J | Oxidized ore, Mineral Joe mine, Colo. | —* | 0·7115 ± 0·0022 | 137·8 ± 0·31 |
| N | Partially oxidized uranium ore, Mineral Joe mine, Colo. | 0·048 ± 0·002 | 0·7118 ± 0·0022 | 137·7 ± 0·31 |
| GS-64 | Fresh uraninite, Happy Jack mine, Utah | 0·048 ± 0·002 | 0·7115 ± 0·0013 | 137·8 ± 0·26 |
| GS-87 | Oxidized ore, Happy Jack mine, Utah | 0·052 ± 0·002 | 0·7115 ± 0·0022 | 137·8 ± 0·31 |
| PK-18 | Carbonaceous ore, Temple Mountain, Utah | 0·055 ± 0·002 | 0·7115 ± 0·0022 | 137·8 ± 0·31 |
| AE-1165 | Fresh unaltered uraninite, Mi Vida mine, Utah | 0·048 ± 0·002 | 0·7119 ± 0·0022 | 137·7 ± 0·31 |
| AE-1260 | Coffinite, Woodrow Pipe mine, New Mexico | 0·064 ± 0·005 | 0·7124 ± 0·0017 | 137·6 ± 0·24 |
| AE-1271 | Coffinite, Poison Canyon mine, New Mexico | 0·143 ± 0·010 | 0·7116 ± 0·0022 | 137·8 ± 0·31 |
| AE-1288 | Oxidized ore, black, J. J. mine, Paradox Valley, Colo. | 0·052 ± 0·002 | 0·7116 ± 0·0022 | 137·8 ± 0·31 |
| PK-2 | Apparently altered uraninite, Joachimsthal | | | |
| PK-5 | Uraninite, Great Bear Lake, Canada | 0·051 ± 0·002<br>0·048 ± 0·002 | 0·7112 ± 0·0020<br>0·7114 ± 0·0018 | 137·8 ± 0·28<br>137·8 ± 0·25 |
| | | | Average Ratio | 137·7 ± 0·32 |

* Not determined.

oxidized ore, and G is low-grade thoroughly oxidized yellow-brown sandstone. S is a composite sample of three channel samples, F, G, and H (F and H being adjacent to and on either side of sample G).

Samples GS-64 and GS-87 are from the Happy Jack mine, San Juan County, Utah. The mine is in the Shinarump member of the Chinle formation of Triassic age. GS-64 has been described by Stieff and Stern (1952) and is, to the authors' knowledge, the freshest, least altered uraninite yet found on the Colorado Plateau.

GS-87 is a composite mill-pulp sample representing tons of altered and oxidized ore from the same mine.

Professor JOHN W. GRUNER of the University of Minnesota has kindly provided the following samples and sample descriptions:

Sample AE-1165 is a specimen of very fresh, unaltered uraninite from the Mi Vida mine, San Juan County, Utah. Montroseite, VO(OH), is also present in the sample.

Sample AE-1260 is a specimen of coffinite, $U(SiO_4)_{1-x}(OH)_{4x}$, from the Woodrow Pipe mine near Laguna, Valencia, County, New Mexico. The mine is in the Morrison formation of Jurassic age. The sample was obtained from the Anaconda Mining Company and is believed to have been collected near the bottom of the shaft, about 80 feet from the surface. The pyrite and marcasite associated with the coffinite are quite fresh.

Sample AE-1271 is a specimen of coffinite from the Poison Canyon mine, McKinley County, New Mexico. The mine is in the Morrison formation. The sample came from a depth of approximately 100 feet below the surface of the ground and contained some slightly reddish material, possibly primary haematite. (The extremely high radium activity ratio of this sample, however, suggests to the authors that it has been subjected to extreme alteration and oxidation as explained below and that the haematite is probably secondary.)

Sample AE-1288 is from the J. J. mine, Montrose County, Colorado. The mine is in the Morrison formation. This ore contained oxidized vanadium minerals and it may be assumed that the uranium minerals had also been oxidized.

Sample PK-18 is from the Temple Mountain district, Emery County, Utah. The mines in this district occur in the Moss Back member of the Chinle formation of Late Triassic age. The sample is representative of the black uranium-bearing carbonaceous ores of the area. In general, this material shows very little evidence of oxidation and alteration.

Sample PK-2 is a specimen of uraninite from the Joachimsthal district, Czechoslovakia, and was obtained from Ward's Scientific Company.

Sample PK-5 is a specimen obtained from the Eldorado Mining Company, Great Bear Lake, Canada. (For description, see KURODA and EDWARDS, 1954.) Additional Great Bear Lake samples from Ward's Scientific Company gave $Ra^{223}/Ra^{226}$ ratios in very close agreement with the value in the table.

With the exception of sample G the $U^{238}/U^{235}$ abundance ratios of all the specimens are within the experimental error of 137·7—the average $U^{238}/U^{235}$ ratio. Some difficulty was experienced in making the analyses of sample G and in preparing the $UF_6$, probably because of impurities present in the ore.

As shown in Table 1 the $Ra^{223}/Ra^{226}$ activity ratios of the samples vary markedly, in contrast to the uniform $U^{238}/U^{235}$ abundance ratio. The calculated activity ratios using the most recent decay constants for $U^{235}$ and $U^{238}$ is 0·046. GS-64 and PK-5, the samples showing the least evidence of alteration, have $Ra^{223}/Ra^{226}$ activity ratios of 0·048. The presence of abundant haematite in sample AE-1271 and the fact that it has the highest-measured activity ratio of the group, namely 0·143, suggests that this sample has been subjected to extensive oxidation and alteration. It would seem, therefore, that the samples with radium activity

ratios greater than 0·048 can be explained by the alteration of the ore and the simultaneous loss of $Ra^{226}$ and $Ra^{223}$ within the last 10,000 years (approximately 6 times the half-life of $Ra^{226}$). Under these conditions $Ra^{223}(T_{1/2} = 11{\cdot}2$ days) and its daughter products will grow back much more rapidly than $Ra^{226}$ and its daughter products. This explanation is reasonable and will explain both the geologic field relations and the observed variation in the activity ratios of radium and its daughter products.

It has been suggested (Kuroda, 1955) that the disagreement between $Pb^{206}/U^{238}$ and $Pb^{207}/Pb^{206}$ ages calculated from the same sample can be reduced by using the measured radium activity ratio instead of the uranium activity ratio of 0·046, on the basis that the variations in the radium activity ratio reflected variations in the $U^{238}/U^{235}$ abundance ratio. Significant variations of $U^{238}/U^{235}$ abundance ratios have not been found in these samples. Continuous selective enrichment of any of the radioactive daughter products between $U^{235}$ and $Ra^{223}$ or selective depletion of the daughter products between $U^{238}$ and $Ra^{226}$ could produce the observed age-discrepancies. Also, periodic loss of radium, throughout a major portion of the sample's history could result in abnormally high $Ra^{223}/Ra^{226}$ ratios. Under these unlikely conditions $Pb^{207}$ would be enriched relative to $Pb^{206}$ and the $Pb^{207}/Pb^{206}$ age would be much greater than the $Pb^{206}/U^{238}$ age.

Loss of radium is not supported by the data on samples GS-64 and PK-5 which show a low $Ra^{223}/Ra^{226}$ activity ratio most nearly approaching the calculated value for the $U^{235}$ and $U^{238}$ series. These two samples still exhibit significant discrepancies between their $Pb^{206}/U^{238}$ and $Pb^{207}/Pb^{206}$ ages (see Table 2).

Table 2. Comparison of $Pb^{206}/U^{238}$ and $Pb^{207}/Pb^{206}$ ages

| Sample No. | Location and description | $Pb^{206}/U^{238}$ age in m.y. | $Pb^{207}/Pb^{206}$ age in m.y. |
|---|---|---|---|
| N* | Relatively fresh ore, Mineral Joe mine, Colo. | 55 | 590 |
| GS-64* | Uraninite, Happy Jack mine, Utah | 65 | 190 |
| GS-87* | Mill pulp, Happy Jack mine, Utah | 230 | 425 |
| N-1† | Uraninite, Joachimsthal, Czechoslavakia | 225 | 214 |
| N-10‡ | Uraninite, Great Bear Lake, Canada | 1251 | 1420 |

* Analysis and age, U.S. Geological Survey.
† Analysis of A. O. Nier (1939b). Age recalculated by A. Holmes (1946).
‡ Analysis and age by A. O. Nier (1939b).

Sample GS-64 shows no mineralogic evidence of oxidation or alteration and therefore no visible mechanism for the continuous removal of radium. It would seem improbable that these samples would be in radium-uranium equilibrium now and yet could have lost significant quantities of radium in the past. Of equal significance, the $Pb^{206}/U^{238}$ and $Pb^{207}/Pb^{206}$ ages on a sample of uraninite from Joachimsthal analysed by A. O. Nier, sample N-1, are essentially in agreement, while the radium-activity ratio of a similar sample from the same locality is high (0·051). Although recent loss of radium can account for the observed $Ra^{223}/Ra^{226}$

activity ratios, it would not measurably affect the $Pb^{207}/Pb^{206}$ ages. Thus, it seems that an alternative explanation for the lead-uranium and lead-lead age discrepancies must be found.

## References


Garrels R. M., Pommer A., Larsen E. S. 3d, and Coleman R. G. Detailed chemical relations in two vanadium-uranium ores, *U.S. Geol. Survey Prof. Paper* (in preparation).

Holmes A. (1946) The construction of a geological time scale, *Geol. Soc. Glasgow Trans.* **21,** 139.

Katz J. J. and Rabinowitch E. (1951) *The Chemistry of Uranium*, New York, McGraw-Hill Book Co., 3-8.

Kuroda P. K. (1955) On the isotopic constitution of radium ($Ra^{223}/Ra^{226}$) in uranium minerals and recent problems of geochronology, *New York Acad. Sci. Annals* **62,** art. 8, 177–208.

Kuroda P. K. and Edwards R. R. (1954) Radiochemical measurements of the natural fission rate of uranium, *J. Chem, Phys.* **22,** 1940.

Nier A. O. (1939a) The isotopic composition of uranium and the half-lives of the uranium isotopes. I, *Phys. Rev.* **55,** 150–153.

Nier A. O. (1939b) The isotopic constitution of radiogenic leads and the measurement of geological time. II, *Phys. Rev.* **55,** 153.

Stieff L. R. and Stern T. W. (1952) Identification and lead-uranium ages of massive uraninites from the Shinarump conglomerate, Utah, *Science* **115,** 706–708.

Stieff L. R., Stern T. W., and Milkey R. (1953) A preliminary determination of the age of some uranium ores of the Colorado Plateau by the lead-uranium method, *U.S. Geol. Survey Circ.* **271,** 19 p.


*Note added in proof:*

M. Lounsbury has recently published a paper describing the measurement of the $U^{235}/U^{238}$ abundance ratio in uranium obtained from Great Bear Lake pitchblende. His value of $137{\cdot}8 \pm 0{\cdot}25$ agrees with the value in this paper of $137{\cdot}8 \pm 0{\cdot}25$ for uranium from the same location.


M. Lounsbury (1956) The natural abundances of the uranium isotopes, *Can. J. Chem.* **34,** 259-264.

Geochimica et Cosmochimica Acta. 1957, Vol. 11, pp. 194 to 199. Pergamon Press Ltd., London

# GEOCHEMICAL NOTES

## Chlorine-36 in pitchblende

(*Received* 4 *August* 1956)

**Abstract**—The natural occurrence of chlorine-36 in pitchblende has been established. The specific activity of chlorine in Great Bear Lake pitchblende, (4 ± 1) disintegrations per minute per gram of chlorine, corresponds to an "apparent thermal neutron flux" of (0·12 ± 0·03) neutrons $cm^{-2}$ $sec^{-1}$.

THE natural occurrence of chlorine-36 (half-life $3{\cdot}08 \times 10^5$ years) has recently been established by DAVIS and SCHAEFFER.[1] They showed that cosmic-ray neutrons induce measurable amounts of chlorine-36 activity in certain surface rocks containing chlorine.

The authors have investigated the occurrence of chlorine-36 in pitchblende, where the major neutron sources are the spontaneous fission of uranium-238 and $(\alpha, n)$ reactions.

Chlorine was isolated from 4540 g of Great Bear Lake pitchblende* (45·3% U and 0·02% Cl) and was purified in the following manner:

Pitchblende was dissolved in dilute nitric acid and the chlorine was precipitated from the filtrate as silver chloride. The nitric-acid insoluble fraction of the pitchblende was treated with (1 : 1) ammonium hydroxide solution and filtered. The filtrate was acidified with nitric acid and the chlorine was precipitated as silver chloride. The silver-chloride precipitate was dissolved in ammonia and the silver was precipitated as silver sulphide by passing hydrogen sulphide gas through the solution. The silver-sulphide precipitate was filtered off and the filtrate was carefully evaporated to dryness in a quartz dish. The residue was treated with a small volume of water and the insoluble residue was filtered off. The filtrate was transferred to a small distillation flask, about 1 ml of concentrated sulphuric acid was added to the solution, and the solution was carefully distilled. The distillate was collected in a small quartz dish, ammonia gas (anhydrous ammonia, MATHESON) was passed through the solution until the solution became alkaline, and the solution was evaporated to dryness.

727 mg of ammonium chloride was recovered from the nitric-acid soluble fraction of the pitchblende and 279 mg of ammonium chloride was obtained from the nitric-acid insoluble fraction. The recovery of chlorine was about 75%.

A screen wall Geiger-Müller counter for radiocarbon dating[2] was used for the radioactivity measurements. The ammonium chloride was dissolved in a few millilitres of water and the solution was evaporated until crystals began to appear on the surface. Then 5 ml of absolute alcohol was poured in rapidly, and a slurry of ammonium chloride was produced. The slurry was centrifuged to the inside wall of the liner by revolving the liner in a lathe.

* A detailed analysis of the Great Bear Lake pitchblende has been reported by J. P. MARBLE (*American Mineralogist* (1939) **24**, 272). The chlorine content was not determined by MARBLE. It is interesting to note that the mineral contains 0·01% of metallic silver. This explains the fact that not all the chloride present in the mineral is extracted by the nitric-acid treatment.

A detailed analysis of the Great Bear Lake pitchblende by MARBLE: $U_3O_8$ 61·56, Pb 10·51, $ThO_2$ 0·00, $SiO_2$ 15·26, CaO 1·44, MgO 0·26, $ZrO_2$ 0·00, CuO 1·11, Ag (metallic) 0·01, MnO 0·00, $Ce_2O_3$ 0·18, $Yt_2O_3$ etc 0·53, $La_2O_3$ etc. 0·53, other rare earths 0·31, $Fe_2O_3$ 1·52, $Al_2O_3$ 0·27, $TiO_2$ 0·05, BaO 0·01, $K_2O + Na_2O$ 1·36, $V_2O_5 + MoO_3$ 1·14, NiO + CoO 2·42, S 0·75, $H_2O(-)$ 0·66, $H_2O(+)$ 0·87.

The counter had a background of 7 c.p.m. in anticoincidence with the surrounding counters.

Table 1 shows the results of radioactivity measurements. To ensure that the activity observed was due to chlorine-36, the ammonium chloride sample was redistilled with sulphuric acid as described earlier, and recounted. No change in counting rate was observed above the counting errors.

The specific activity of chlorine in Great Bear Lake pitchblende, $(4 \pm 1)$ disintegrations per minute per gram of chlorine, corresponds to an "apparent thermal neutron flux" of $(0{\cdot}12 \pm 0{\cdot}03)$ neutrons $cm^{-2}$ $sec^{-1}$.

Table 1. Counting data on ammonium chloride extracted from Great Bear Lake pitchblende

| Sample on liner | Counting rate (c.p.m.) | Specific activity (d.p.m. per gram Cl) |
|---|---|---|
| 577 mg ammonium chloride, Great Bear Lake pitchblende | $0{\cdot}75 \pm 0{\cdot}12$ | $4{\cdot}1 \pm 0{\cdot}7$ |
| 232 mg ammonium chloride, Great Bear Lake pitchblende, twice-distilled | $0{\cdot}30 \pm 0{\cdot}10$ | $4{\cdot}0 \pm 1{\cdot}3$ |
| 6500 mg ammonium chloride, analytical reagent | $0{\cdot}03 \pm 0{\cdot}09$ | $0{\cdot}01 \pm 0{\cdot}03$ |
| 500 mg ammonium chloride, containing 51·3 d.p.m. chlorine-36 | $25{\cdot}1 \pm 1{\cdot}4$ | 155 (standard) |

Assuming that thermal capture is the ultimate fate of each neutron produced, the ratio of induced fission vs. spontaneous fission in this mineral can be estimated from the following equation:

$$\frac{\text{Number of chlorine-36 disintegrations per min per g mineral}}{\text{Number of induced fission per min per g mineral}} = \frac{N^{35}(\sigma_a)_{35}}{N^{235}(\sigma_f)_{235}} \qquad (1)$$

where, $N^{35}$ and $N^{235}$ are the number of atoms of chlorine-35 and uranium-235 per gram of mineral, respectively, $(\sigma_a)_{35}$ is the thermal neutron absorption cross-section of chlorine-35, and $(\sigma_f)_{235}$ is the thermal fission cross-section of uranium-235.

A value of $(3{\cdot}4 \pm 0{\cdot}8) \times 10^{-2}$ is obtained for the number of induced fissions per minute per gram of this mineral.

The number of spontaneous fissions per minute per gram of this mineral can be calculated from the spontaneous fission half-life of uranium-238 and the uranium-238 content of the mineral. The spontaneous fission half-life given by Segrè (1952), $(8{\cdot}04 \pm 0{\cdot}3) \times 10^{15}$ years, yields a value of 0·188 spontaneous fissions per minute per gram of this mineral, and the spontaneous fission half-life of Perfilov (1947), $(1{\cdot}3 \pm 0{\cdot}2) \times 10^{16}$ years, yields a value of 0·116 spontaneous fissions per minute per gram mineral. Thus, the ratio of induced fission to spontaneous fission in this mineral is $(18 \pm 4)\%$ based on Segrè's half-life value, and $(29 \pm 7)\%$ based on Perfilov's half-life value. These results seem to agree fairly well with the estimates made by previous workers based on the entirely different methods. The results of the mass-spectroscopic measurements of the xenon isotopes in minerals by

Fleming and Thode (1953) indicate that the ratio of induced fission to spontaneous fission in Great Bear Lake pitchblende (a mill concentrate; original uranium content unknown) to be approximately 10%. Wetherill (1953) reported that about 35% of the fission in Belgian Congo pitchblende (44% U) is neutron-induced, while Kuroda and Edwards (1954) found that about 27% of the fission in Great Bear Lake pitchblende (35% U) is neutron-induced.

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References

Davis R. jr. and Schaeffer O. A. (June 1955) *BNL* 340(T-59).
Fleming W. H. and Thode H. G. (1953) *Phys. Rev.* **92,** 378.
Kuroda P. K. and Edwards R. R. (1954) *J. Chem. Phys.* **22,** 1940.
Libby W. F. (1952) *Radiocarbon Dating*, University of Chicago Press.
Perfilov N. A. (1947) *J. Expt. Theoret. Phys.* U.S.S.R. **17,** 476; *Chem. Abstracts* **42,** 2864.
Segrè E. (1952) *Phys. Rev.* **86,** 21–28.
Wetherill G. W. (1953) *Phys. Rev.* **92,** 907.

## Chemical energy and metamorphism: a discussion

In a recent paper, Saull (1955) discusses the interesting idea that metamorphic neomineralization and recrystallization are largely exothermic processes, the source of the released heat being solar energy stored in the weathering products. Saull considers three types of chemical processes: (1) devitrification, (2) recrystallization, (3) chemical reactions. Devitrification of a glass is admittedly exothermic, but glass is hardly abundant enough in sediments to make this thermal effect significant. If recrystallization means change from very fine-grained material to a coarse-grained aggregate without phase change, this process is also exothermic, particularly if the original material is of colloidal size. In terms of thermal energy, however, the chemical mineral reactions are the more important. It is not very likely that such reactions are exothermic when a sediment changes to a metamorphic rock (provided that the system is closed). This is obvious if the products of weathering and sedimentation are stable at the low surface-temperature of the earth. Under such conditions, increasing temperature permits only endothermic reactions to take place. If the products of weathering and sedimentation are metastable under surface conditions, a release of heat is possible when more stable mineral assemblages form. It is probable that some diagenetic processes are exothermic for this reason. Moreover, sedimentation piles together material from various sources, thus frequently creating unstable mineral assemblages. It seems reasonable, however, that any exothermic chemical adjustment which may result from this condition is essentially completed during diagenesis, and therefore is of little significance as heat source during regional metamorphism.

In a list of twenty reactions, Saull attempts to show that the formation of metamorphic minerals from products of weathering and sedimentation is in general exothermic. Among

SAULL's examples, Nos. 19: $CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2$, and 20: $Al_2Si_2O_5(OH)_2 \rightarrow Al_2SiO_5 + SiO_2 + H_2O$, are the only realistic mineral reactions. No. 19 is strongly endothermic (although less so than recorded by SAULL; see Table 1 below) and is thus in opposition to SAULL's hypothesis. This could be considered an exception, because wollastonite is essentially a contact metamorphic mineral. The same cannot, however, be claimed for other carbonate-silicate reactions, which produce typical regional-metamorphic minerals but yet are strongly endothermic, as shown in Table 1.

Table 1. Enthalpy changes for metamorphic reactions*

| Reaction | $\Delta H_{298}$ (kcal) | References |
|---|---|---|
| Dolomite + 2 quartz = diopside + $2CO_2$ | +37·0 | WEEKS (1956a) |
| 2 dolomite + quartz = 2 calcite + forsterite + $2CO_2$ | +44·2 | Do. |
| Dolomite + quartz = calcite + enstatite + $CO_2$ | +21·0 | Do. |
| Calcite + quartz = wollastonite + $CO_2$ | +21·2 | DANIELSSON (1951) WEEKS (1956a) |
| Dolomite = calcite + periclase + $CO_2$ | +29·7 | WEEKS (1956a) |
| Diopside + forsterite + 2 calcite = 3 monticellite + $2CO_2$ | +52·7 | Do. |
| Forsterite + calcite = monticellite + periclase + $CO_2$ | +30·1 | Do. |
| Diopside + calcite = akermanite + $CO_2$ | +33·9 | Do. |
| Calcite = lime + $CO_2$ | +42·5 | Do. |
| Magnesite + quartz = enstatite + $CO_2$ | +19·4 | Do. |
| 2 magnesite + quartz = forsterite + $2CO_2$ | +41·1 | Do. |
| Magnesite = periclase + $CO_2$ | +28·1 | Do. |
| Rankinite + calcite = 2 larnite + $CO_2$ | +36·9 | Do. |
| Diopside + 2 calcite = merwinite + $2CO_2$ | +63·2 | Do. |
| Brucite = periclase + $H_2O$ | +8·84 to +9·73 | ROSSINI *et al.* (1952) |
| Anthophyllite = 7 enstatite + quartz + $H_2O$ | +12·0 | WEEKS (1956b) |
| Tremolite = 2 diopside + 3 enstatite + quartz + $H_2O$ | +24·3 | Do. |
| Tremolite + 3 calcite + $2SiO_2$ = 5 diopside + $3CO_2$ + $H_2O$ | +72·1 | Do. |
| Tremolite + 11 dolomite = 8 forsterite + 13 calcite + $9CO_2$ + $H_2O$ | +241·1 | Do. |
| Serpentine + brucite = 2 forsterite + $3H_2O$ | +18·4 | BENNINGTON (1955) |
| 5 serpentine = 6 forsterite + talc + $10H_2O$ | +71·4 | Do. |
| Talc + forsterite = 5 enstatite + $H_2O$ | +7·2 | Do. |
| Talc = 3 enstatite + quartz + $H_2O$ | +9·5 | Do. |

* $+\Delta H$ means endothermic, $-\Delta H$ exothermic reactions.

Reaction (20) is probably the most significant of those considered by SAULL, because it represents a realistic transformation of a common clay mineral, kaolinite, to common metamorphic minerals, sillimanite and quartz. If this reaction is as pronouncedly exothermic as assumed by SAULL (−26 kcal), he indeed has strong support for his hypothesis. Unfortunately, there are good reasons to assume that the enthalpy change of reaction (20) is in error by a very large amount. SAULL bases the −26 kcal on heats of formation given for sillimanite by KLEVER (see reference in SAULL's paper), who in turn employs heat-of-solution values measured by NEUMANN (1925). There are at least three independent

conditions which show that the reported $\Delta H$ value for sillimanite (kyanite and andalusite also, for that matter) must be greatly in error.

(1) Crystal-energy theories predict that the heat of formation of any modification of $Al_2SiO_5$ from the oxides (i.e. $Al_2O_3 + SiO_2 = Al_2SiO_5 + \Delta H_{298.16}$) should be much smaller than the $-37$ to $-50$ kcal quoted in literature by KUBASCHEWSKI and EVANS 1951; KLEVER, *op. cit.*; EITEL, 1952, and others. A value around $-10$ kcal is much more probable on these grounds, as discussed by one of us (H. R., 1953).

(2) NEUMANN's claim of having dissolved sillimanite, kyanite, and andalusite in 40% HF in the course of less than 15 min at room temperature seems unlikely, in view of other attempts to dissolve these minerals. Fine powder of kyanite showed no sign of attack by 20% HF in the course of $\frac{1}{2}$ hour at 80°C in our calorimeter at The University of Chicago. (NEUMANN ground his sample for 100 hours in an agate mill. It is possible that the heat effect in the calorimeter was due to silica from the mill.)

(3) The large $\Delta H$ values given for the various modifications of $Al_2SiO_5$ can not be reconciled with the experimental equilibrium curves of the following mineral reactions:

$$\underset{\text{muscovite}}{KAlSi_3AlO_{10}(OH)_2} \rightleftharpoons \underset{\text{orthoclase}}{KAlSi_3O_8} + Al_2O_3 + H_2O \qquad (1)$$

and

$$\underset{\text{paragonite}}{NaAlSi_3AlO_{10}(OH)_2} \rightleftharpoons \underset{\text{albite}}{NaAlSi_3O_8} + Al_2O_3 + H_2O \qquad (2)$$

as measured by EUGSTER and YODER (1954). The equilibrium curves show that the above reactions must have $\Delta H$ values close to that of the brucite-periclase reaction, i.e. around $+9$ kcal per mol (ROSSINI *et al*, 1952), as shown in Table 1. (The brucite $\rightleftharpoons$ periclase + water equilibrium curve as measured by ROY, ROY, and OSBORN, (1953) falls very close to the mica curves of EUGSTER and YODER. Since all reactions involve 1 mol of $H_2O$ and the major portion of the entropy change is associated with the fluid water phase, identical equilibrium curves should correspond to rather similar $\Delta H$ values.)

If silica is added to one of the reactions above, sillimanite (kyanite or andalusite) will occur on the right-hand side under equilibrium conditions:

$$\underset{\text{muscovite}}{KAl_2Si_3AlO_{10}(OH)_2} + SiO_2 \rightleftharpoons \underset{\text{orthoclase}}{KAlSi_3O_8} + \underset{\text{sillimanite}}{Al_2SiO_5} + H_2O \qquad (3)$$

The heat of this reaction is the sum of the heat of reaction (1) and the heat of formation of sillimanite from the component oxides. $\Delta H_{298.16}$ for reaction (1) is about $+9$ kcal, so if the heat of formation of sillimanite really is $-48$ kcal, as assumed by SAULL, we find that reaction (3) is exothermic by no less than $-39$ kcal. Since the right side of reaction (3) contains free water, this side is also the high-entropy side at temperatures above the stability field of ice, except possibly at very high pressures. This means that the entropy change of the reaction is positive which, combined with negative $\Delta H$, gives negative free-energy change at all P-T conditions outside the stability field of ice and extremely compressed water, according to the "second law":

$$\Delta F = \Delta H - \Delta ST$$

Consequently, muscovite should be unstable in association with silica, except perhaps at extreme pressures and/or at temperatures at which ice is stable. There is no doubt, however, that muscovite and quartz exist stably together over a very wide temperature-pressure range in nature. This requires that the unknown heat of formation of sillimanite is such that reaction (3) be endothermic (i.e. positive $\Delta H$), so that $\Delta F$ can be positive. The following condition must therefore be satisfied:

$$\Delta H_{\text{sillimanite}} > -\Delta H_{\text{reaction(1)}}$$

where $\Delta H_{\text{reaction(1)}}$ is about 9 kcal. Such a value for $\Delta H_{\text{sillimanite}}$ will change the kaolinite reaction (20) from strongly exothermic, as assumed by SAULL, to appreciably endothermic.

The heats of other hydration-dehydration reactions in the system MgO, $SiO_2$, $H_2O$ have been determined by one of us (K. B.). As shown in Table 1, these reactions are also endothermic in the direction of the assemblages containing free water, as one should expect.

There is thus neither factual nor theoretical support for the assumption of SAULL, that closed-system regional metamorphism of sedimentary rocks is generally exothermic.

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## REFERENCES

BENNINGTON K. O. (1956) Role of shearing stress and pressure in differentiation as illustrated by some mineral reactions in the system MgO—$SiO_2$—$H_2O$. *J. Geol.* **64,** 558–577.

DANIELSSON A. (1951) Das Calcit-Wollastonit-Gleichgewicht. *Geochim. et Cosmochim. Acta* **1,** 55–69.

EITEL W. (1952) *Thermochemical Methods in Silicate Investigation.* Rutger University Press, New Brunswick, New Jersey.

EUGSTER H. and YODER H. S. (1954) Annual Report of the Director of the Geophysical Laboratory, Washington.

KUBASCHEWSKI O. and EVANS E. LL. (1951) *Metallurgical Thermochemistry,* Butterworth-Springer, Ltd., London.

NEUMANN F. (1925) Über die Stabilitätsverhältnisse der Modifikationen in polymorphen System $Al_2SiO_5$. *Z. anorg. Chem.* **145,** 193–238.

RAMBERG H. (1953) Heats of reaction among solids as related to properties of constituent ions. *J. Geol.* **61,** 318–352.

ROSSINI F. D., WAYMAN D. D., EVANS W. H., LEVIN S., and JAFFE I. (1952) Selected values of Chemical Thermodynamic Properties, Circular of the Nat. Bur. of Stands., No. 500.

ROY D. M., ROY R., and OSBORN E. (1953) The system MgO—$Al_2O_3$—$H_2O$. *Amer. J. Sci.* **251,** 337–361.

SAULL V. A. (1955) Chemical Energy and Metamorphism. *Geochim. et Cosmochim. Acta* **8,** 86–106

WEEKS W. F. (1956a) A thermochemical study of equilibrium relations during metamorphism of siliceous carbonate rocks. *J. Geol.* **64** 245–270.

WEEKS W. F. (1956b) The heats of formation of metamorphic minerals in the system CaO—MgO—$SiO_2$—$H_2O$ and their petrological significance. *J. Geol.* **64** 456–472.

# LETTERS TO THE EDITORS

## Terrestrial helium

(*Received* 9 *September* 1956)

In a recent issue of this journal (April), Dr. Mayne (1956) has presented an argument for a tenfold terrestrial increment of $He^3$ from extra-terrestrial dust. The argument proceeds as follows. Assuming that the earth's crust is composed of $15 \times 10^{24}$ g granite containing 4·2 p.p.m. uranium and $7{\cdot}5 \times 10^{24}$ g basalt containing 0·6 p.p.m. uranium, the Th/U ratio in the crust is 3·5 and the rate of release of helium from the crust is equal to the rate of generation, then, according to these calculations and assumptions the rate of liberation must be sixty times the original estimate based upon rock erosion. Now, if this is the case, the rate of loss from the exosphere must be much greater to maintain the measured atmospheric helium content and likewise the rate of $He^3$ production must be about tenfold greater than previous estimates from fast-neutron reactions and spallation in the atmosphere. Mayne identifies the source as extra-terrestrial dust amounting to 10,000 tons a day, more or less, and suggests this hypothesis can be verified by sampling and analysing arctic snow for its $He^3/He^4$ ratio.

It appears to the writer of this letter that the tenfold extra-terrestrial increment of $He^3$ demanded by Dr. Mayne's calculations is based upon an overestimation of (1) the specific helium productivity of uranium and thorium, (2) the helium production in the earth's crust, (3) the rate of loss of helium from the crust to the atmosphere. Firstly, the specific helium production in units of microlitres ($10^{-3}$ s.c.c) per $M_x$ g per $t$ years is given by the following equation:

$$\mathrm{He} = \frac{N_A}{A_x} K_x M_x (e^{\pi_x t} - 1)$$

where $N_A$ = atomic volume in microlitres at STP, $22{\cdot}4 \times 10^6$ microlitres.
$A_x$ = atomic weight = 238, 235, and 232 for $U^{238}$, $U^{235}$, and $Th^{232}$ respectively.
$K_x$ = number of alpha particles emitted per complete transformation from initial parent isotope to final end product in the respective series.
$M_x$ = weight of initial parent of series at present time in grams.
$\pi_x$ = the decay constants $1{\cdot}537 \times 10^{-10}\ \mathrm{yr}^{-1}$, $9{\cdot}720 \times 10^{-10}\ \mathrm{yr}^{-1}$, and $0{\cdot}4985 \times 10^{-10}\ \mathrm{yr}^{-1}$ for $U^{238}$, $U^{235}$, and $Th^{232}$ respectively.

Solving, the production rates in units of microlitres per microgram per $10^9$ years are:

| | |
|---|---|
| $U^{238}$ | 0·125 |
| $U^{235}$ | 0·00796 |
| $Th^{232}$ | 0·0296 |

for the value of 4·2 p.p.m. uranium ($1{\cdot}4 \times 10^{-12}$ g Ra) per gram of granitic rock and a Th/U ratio of 3·5 used by Mayne we have the following helium production in microlitres per gram of granite per $10^9$ years:

| | |
|---|---|
| $U^{238}$ | 0·526 |
| $U^{235}$ | 0·033 |
| $Th^{232}$ | 0·436 |
| | 0·995 |

which is lower by a factor of 3·5 than the value of $3{\cdot}5 \times 10^{-3}$ cm$^3$/g used by MAYNE in his calculations.

Secondly, the average composition of surface continental rocks is not granitic in composition, but granodioritic (e.g. see POLDERVAART 1955). Furthermore, the mean density of 2·84 for the crust (WORZEL and SHURBET, 1955) indicates that subsurface rocks are more basic than granite. Therefore, the use of a value for the radioactivity of the continental crust (with the exception of a 5-km basalt layer) equivalent to granite is not justified. If the radioactivity of granodiorite* is substituted for that of granite, the crustal helium production rate is reduced by a factor of 1·9.

Thirdly, according to KEEVIL (1941) the helium retentivity for granitic rocks and basaltic rocks of all ages and conditions has a mean value of 0·28 and 0·46 respectively. In this paper and in a subsequent paper, KEEVIL (1950) has presented evidence that the helium retentivity is a function of the extent to which the rock has been altered. The rocks used in retentivity studies have been through all of the vicissitudes of exposure and subsequent weathering. Nevertheless, use of these low retentivities† for the crust as a whole would still lower the rate of helium loss by an additional factor of about 1·7.

If the helium-leak rate into the atmosphere, used by MAYNE, is then reduced by the factor $3{\cdot}5 \times 1{\cdot}9 \times 1{\cdot}7 = 11$, the necessity of hypothecating a large extra-terrestrial source of $He^3$ is removed. Unquestionably, some extra-terrestrial dust is swept up by the earth, but it is probably much less than the 10,000 tons a day called for by MAYNE. Sampling arctic snow for $He^3$ containing dust seems to the writer to be an excellent proposal, but it is essential that the quantity of snow to be sampled should not be underestimated.

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## REFERENCES

KEEVIL N. B. (1941) The unreliability of the helium index in geological correlations, University of Toronto Studies, Geol. Series, No. 46, pp. 39–67.

KEEVIL N. B. (1950) Radioactivity and mineral deposits, *Amer. Min.* **35,** 816–833.

MAYNE K. I. (1956) *Geochim. et Cosmochim. Acta* **9,** 174.

POLDERVAART A. (1955) Chemistry of the earth's crust, G.S.A. Special Paper **62,** pp. 119–144.

WORZEL J. L. and SHURBET G. L. (1955) Gravity interpretations from standard oceanic and continental crustal sections, *ibid*, pp. 87–100.

* 2·1 p.p.m U,Th/U = 3·5.
† ~ 40% retentivity used in calculation.

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## Terrestrial helium: a reply

(*Received* 8 *October* 1956)

DR. DAMON has been good enough to let me have a typescript of his letter before publication, concerning my article on "Terrestrial helium" (1956). His lucid calculation of the specific helium productivity of uranium and thorium is, of course, correct (although he is wrong in saying that I require a daily infall of extra-terrestrial dust of 10,000 tons; the figure I suggested—see abstract—is 5000 tons). Nevertheless, I feel that his calculation of the rate of leakage of helium-4

into the earth's atmosphere represents an unjustifiably simple view of the problem of degassing the earth's crust.

It must remain difficult to estimate with any precision the amount of helium which is being released from the crust, until the extent and distribution of the radioactivity of the earth are better known. One can only hope that, by constructing a crude model which represents the gross effects of degassing, it may be possible to obtain an estimate better than an order of magnitude. The model which I have used is one of continuous orogeny, such that the upper crust (down to about 5 km in the basalt layer underlying the continental granite blocks) *as a whole* is being continuously degassed; i.e. there is no buildup there of gaseous radioactive end-products in geological time, and hence the rate of leakage of gas from it is just equal to the rate of accumulation. This is essentially the model of SHILLIBEER and RUSSELL, which they have used to estimate the age of the earth, by assuming atmospheric argon to be entirely radiogenic. The fact that minerals retain (temporarily, in the geological time-scale) some radiogenic helium, by reason of which they may be dated, does not invalidate the gross effect of the continuous degassing process, any more than the retention of some radiogenic argon does. Thus, the question of helium retentivity is not relevant. Nevertheless, let us examine the limitations of this model, particularly as regards the amount and distribution of uranium and thorium; modern measurements suggest that previous determinations are too high.

The total amount of uranium which has been assumed is about $6{\cdot}5 \times 10^{19}$ g, and this has been taken as confined to the 5-km basalt layer and the continental blocks. UREY (1955) has recently considered the question of the uranium and thorium abundance from the point of view of the heat balance of the earth. He has estimated that the total amount of uranium should not exceed about $5 \times 10^{19}$ g, without reference to its distribution, except that this should not go too deeply. The Th : U ratio is taken as 3·5. Thus the present model is high in uranium and thorium by no more than 30%. The question of the distribution of the radioactivity still remains.

While it is true that the radioactive elements will tend to be concentrated upwards, it is surely an over-simplification to assume that they are all concentrated in the upper crust. Thus, helium will be generated below this upper crust, into which it will eventually find its way by diffusion, whence it will be degassed into the atmosphere. The time-constant for the diffusion process is given by $\tau \sim l^2/2D$, where $l$ is the path-length and $D$ the diffusion constant. This latter we may take to be of the order of $10^{-5}$, the helium being in effect in solution in the rock at the pressures obtaining. Thus, helium originating close to the base of the crust, the Moho discontinuity, at the beginning of geological time is being made available at the upper crust at the present. The rate of generation of helium $4{\cdot}5 \times 10^9$ years ago was 3·5 times the present rate.

On the present model, the diffusion contribution is to be added to the present day rate of radiogenic production in the upper crust to give the total accumulation rate there. However, since no assumptions have been made about the lower crust, and hence it is impossible to say what its contribution would be, as a simplification of the model I have taken the total accumulation rate of helium in the upper crust to be 3·5 times the present radiogenic production rate. Now, this simplification overestimates the helium production, because it assumes that more uranium (and thorium) underlie the $6{\cdot}5 \times 10^{19}$ g of the upper crust. The extent of the overestimate is easily seen to be a factor of approximately 1·7. For, suppose that the $6{\cdot}5 \times 10^{19}$ g of uranium is distributed over the whole of the crust and not just the upper 5 km, then the total accumulation rate in the upper crust is approximately the mean production rate over the last $4{\cdot}5 \times 10^9$ years; i.e. about twice the present day rate (the factor for thorium is 1·13). If the distribution is uniform, the factor is less.

If we now adopt UREY's lower value for uranium and thorium abundances, the original estimate for the number of helium-4 atoms liberated per $cm^2$/sec from the earth's surface is to be reduced by a factor 2, giving a leakage of $4{\cdot}5 \times 10^6$ atoms $He^4/cm^2$/sec. This would indicate an infall of extraterrestrial dust of 2000 tons/day, assuming that the helium isotopes have an equal probability of escape from the atmosphere. If helium-3 is lost more rapidly than this, then a greater infall would be required. However, if escape occurs at a high temperature, as suggested, the difference in the escape probabilities of the two isotopes may be no more than 30%, being determined by the relative rates of diffusion to the escape layer. The figure of 2000 tons/day is probably a low estimate, and is in reasonable agreement with the former value.

Dr. Damon's last sentence is indeed germane. Apart from any uncertainty in the total amount of the dust infall, the meteorological factors affecting the dust content of antarctic snow are virtually unknown. Only a pilot investigation will show just how much ice will have to be sampled.

K. I. Mayne

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## References

Mayne K. I. (1956) *Geochim. et Cosmochim. Acta* **9**, 174.
Urey H. C. (1955) *Proc. Nat. Acad. Sci.* **41**, 127.

# ANNOUNCEMENT

## Symposium on Geochemistry

THE Commission on Geochemistry of the International Union of Pure and Applied Chemistry is arranging, on 22, 23, and 24 July 1957, a Symposium on Geochemistry in Paris. This Symposium will be held in conjunction with the XVIth International Congress of Pure and Applied Chemistry, 18–24 July 1957.

A two-day field excursion to the volcanic area of the Auvergne will be held after the Symposium, and a dinner will be arranged for the members during the Symposium.

Prospective members are requested to send in their applications to Professor E. RAGUIN, École des Mines, 60, Boulevard Saint-Michel, Paris 6e.

Members wishing to present scientific papers (time allotted is 15 minutes per paper) are requested to submit the titles to Professor RAGUIN at a very early date. An abstract of the paper not exceeding 250 words in length must be sent to Professor RAGUIN by 1 May 1957. The abstracts will be mimeographed and issued to the members on the opening of the Symposium.

No registration fee will be charged. The cost of the dinner and the field trip will be announced at the time of the opening of the Symposium.

It is strongly advised that the members register for the Congress, asking to obtain the pertinent circulars in order to take advantage of the help of the Union in obtaining accommodation at a time when a large number of visitors will be in Paris and to be able to participate in the extensive social programme during the Congress. All correspondence concerning the Congress should be addressed to Secrétariat du XVIe Congrès International de Chimie, 28, rue Saint-Dominique, Paris 7e.

KALERVO RANKAMA
*Secretary*
*Commission on Geochemistry*

# ANNOUNCEMENT

## GEOCHIMICA ET COSMOCHIMICA ACTA

In order to ensure rapid publication of the large numbers of papers submitted for publication, the journal will this year be published in three volumes of four issues each. The four issues of each volume will contain the same number of pages hitherto spread over six issues.

As soon as the back-log of papers awaiting publication has been reduced, the journal will be able to provide publication of full-length papers within ninety days of acceptance, and short communications within sixty days.

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It is in those branches of natural science which border older established disciplines that the need for critical survey reviews of progress has become greatest. This has arisen partly because subjects such as geochemistry and geophysics fringe and overlap so many other fields and partly because they are at present vigorous growing points in science. A principal aim of the annual series, Chemistry and Physics of the Earth, will be to provide authoritative and up-to-date surveys of progress for those actively engaged in geophysics and geochemistry. But it is hoped also that much of what is written will encourage the interest of the chemist and physicist in a study of our planet, not merely for its own sake, but because such a study often turns out to be of benefit to physics and chemistry. Another aim is to acquaint the geologist with the results and methods of geophysics and geochemistry, particularly as progress in earth science has been hindered by some lack of liaison between different groups. An attempt will be made to provide a balanced variety of topics with roughly equal emphasis on chemistry and physics, but certain topics will be considered fairly regularly.

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